STANDARD CELLS AND THE CHANGE FROM INTERNATIONAL TO ABSOLUTE ELECTRICAL UNITS[1]

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The standard cell which appears on the badge of our society is the fundamental standard for the measurement of electromotive force. Together with standards of resistance it is used also for the precise measurement of current, power and energy. When measurements of electric power are made in terms of standards of electromotive force and resistance the expression for power, $P = \frac{E^2}{R}$, shows the necessity for knowing the electromotive force accurately since an error in the standard for E would produce a percentage error twice as great in the value for power. Electrical engineers and physicists are naturally concerned with the unit of electromotive force, the volt. Equally important is the interest of physical and electrochemists in electromotive force, particularly as it applies to a variety of cells and to equations for the free energy of reactions. Any change in the unit, therefore, is of importance to all who are engaged in precise measurements.

In pursuance of decisions of the International Committee on Weights and Measures, the National Bureau of Standards introduced as of January 1, 1948, revised values of the units of electricity. The object of this paper is to review briefly the development of electrical units during the past century and to indicate why a change is being made at this time and how much the units are altered.

About 1851 Weber, a German, proposed a system of electrical units based upon units of length, mass and time with the further assumption that all experiments were made in a medium of unit permeability. To give substance to his proposal he outlined certain methods by which electrical measurements could be made in terms of the mechanical units of length, mass and time. Theoretically this was most important, but practically the difficulties of making precise electrical measurements in terms of mechanical units were very great. A Committee of the British Association for the Advancement of Science adopted Weber's proposal in 1860 and since then this has formed the basis or at least the background for electrical units.

Weber's principle would permit a system of units to be based either on electrostatics, that is, on the mechanical force between electric charges at rest, or on the magnetic effects which are produced by electric currents. The latter is the basis generally used and by this principle electrical measurements are made concordant with measurements in other fields of science and engineering.

Measurements made on the basis of the fundamental quantities of length, mass and time are called "absolute measurements" in contradistinction to measurements based purely on material standards, arbitrarily defined.

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The latter have been commonly referred to as "international units" because they were established by international agreement, but the absolute units are just as much international in their scope and application.

The difficulties of making precise measurements according to Weber's system led to the use of various physical standards including the column of mercury for the ohm, the silver voltameter for the ampere and the standard cell for the volt. Prior to 1893 these standards were largely the development of individual laboratories. Results differed and a basis of common understanding was lacking.

A bulletin No. 30 entitled "Units of Electrical Measure" was issued in 1893 by the Coast and Geodetic Survey, which at that time was the custodian of weights and measures of this country. It said, "Within but little more than a decade, practical applications of electricity have developed with a rapidity unparalleled in the history of modern industry . . . , but

FIG. 1. Official delegates to the International Electrical Congress held at Chicago 1893. (Courtesy of "Weston Engineering Notes.")

there has been lacking, up to the present time (1893), the very important and essential element of fixed and invariable units of measure authoritatively adopted." An electrical congress comprising official delegates from various countries met at the World's Fair in Chicago in 1893 and agreed upon definitions for fundamental electrical units which recognized in principle the absolute system of Weber but provided for concrete standards to represent them. The standard for the volt selected at that time was the Clark cell, since displaced by the Weston cell. The International Committee which took this action included many celebrated men who are shown in the photograph, Fig. 1.

As time went on greater accuracy of the standards was needed and at the International Conference on Electrical Units and Standards in London in 1908, definitive action was taken recognizing the absolute system of electrical units, but establishing as a separate and independent system the so-called international units based on concrete standards: the mercury ohm,

the silver voltameter and the standard cell. At this time the Weston cell officially replaced Clark's cell. Standards for the ohm and the ampere were considered the two fundamental instruments and the Weston Normal Cell received a value derived from these by Ohm's law. At the time this was stated provisionally to be 1.0184 international volts at 20°C. This figure was somewhat uncertain and provision was made for an international committee to carry out cooperative experiments and to determine a more precise value to be assigned to the Weston Normal Cell, Fig. 2. The International Committee in turn provided for a technical committee to make the experiment. This technical committee consisted of: Sir Frank Smith, National Physical Laboratory, England; Professor F. Laporte, Laboratoire Central d'Électricité, France; Professor W. Jaeger, Physikalisch Technische Reichsanstalt, Germany; Dr. S. W. Stratton, Director, National Bureau of Standards; Dr. E. B. Rosa, Chief Physicist, National Bureau of Standards; Dr. F. A. Wolff, Physicist, National Bureau of Standards. Of these, only

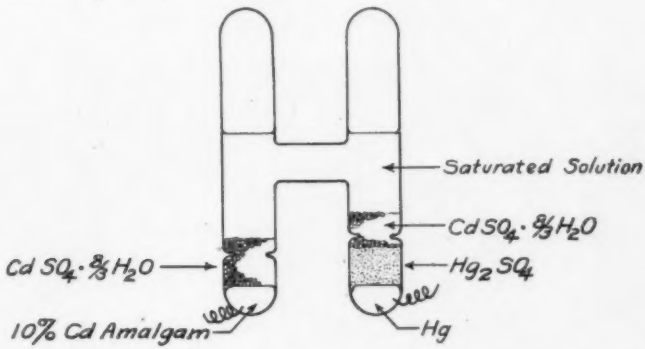

FIG. 2. The saturated, cadmium standard cell. (Weston Normal Cell)

Sir Frank Smith survives. The Committee met at the Bureau of Standards in Washington in April and May, 1910. Members of this committee together with assistants at the Bureau are shown in the photograph, Fig. 3. An agreement was reached at that time as to the value for the international ohm, based on previous measurements of the mercury ohm in England and Germany, but represented by wire resistors. The silver voltameter was used in connection with the adopted standard of resistance and the electromotive force of the Weston Normal Cell was determined to be an average round figure of 1.0183 international volts at 20°C.

By international agreement effective January 1, 1911 the system of international units was recognized, but for practical purposes it was necessary that the units be carried forward on the basis of concrete standards of wire resistors and standard cells. No further adjustment to the values then established has been made in this country until the present time.

Subsequent measurements of the ohm and the ampere have revealed differences between the units as realized from these concrete standards and the absolute units on the basis of length, mass and time. In the case of

the ohm the discrepancy was much larger than was realized in 1910. Precise electrical measurements of the present day make it very desirable, therefore, that a readjustment in our electrical units should be made to bring them into accord with units of measurement in other branches of science and engineering.

This step has not been taken without mature deliberation. As far back as 1927 a proposal for such a change in the units was initiated by a committee of the American Institute of Electrical Engineers and by formal

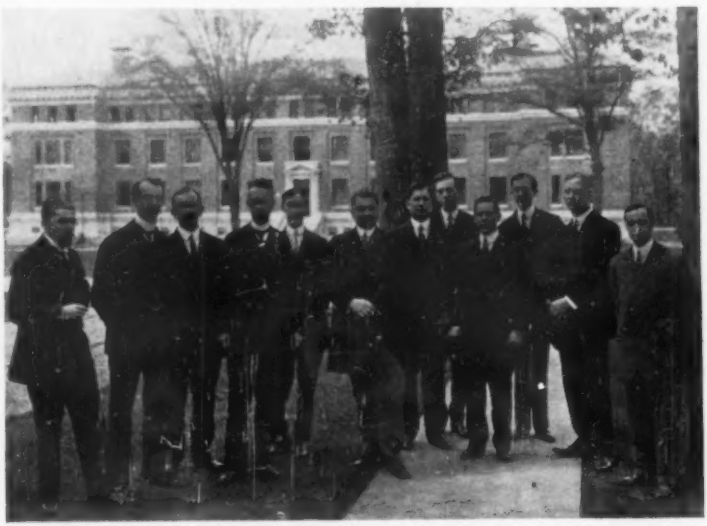

FIG. 3. Members (*) of the International Technical Committee of 1910 and assistants at the National Bureau of Standards. Left to right. F. Laporte* of France Sir Frank Smith* of England, Dr. F. A. Wolff*, Dr. W. Jaeger* of Germany, M. P Shoemaker, Dr. S. W. Stratton*, Director NBS, Dr. F. Wenner, Dr. A. S. McDaniel G. E. Post, Dr. F. W. Grover, Dr. E. B. Rosa*, Dr. G. W. Vinal.

action of the Institute's Board of Directors in 1928 the following resolution was adopted:

> Whereas the legalization of the absolute ohm and ampere and the units derived from them (these units to be realized by the national standardizing laboratories) would avert the recurring proposals for revision of the values of the legalized units, and would establish the electrical units on a permanent legal basis: Therefore be it
>
> Resolved, That the American Institute of Electrical Engineers hereby urges the Bureau of Standards and foreign national standardizing laboratories to undertake as soon as possible the additional researches necessary in order that the absolute ohm and absolute ampere based on the centimeter-gram-second electromagnetic system, with the absolute volt, watt, and other units derived from them, may be legalized in place of the international ohm and ampere and their derived units.

Research work on this subject has been carried on at the National Bureau of Standards, (NBS), and at the other national standardizing laboratories.

In this connection the NBS consulted an Advisory Committee consisting of representatives named by the National Academy of Sciences, the American Institute of Electrical Engineers, the American Physical Society, the National Electric Light Association, the Association of Edison Illuminating Companies, the National Electrical Manufacturers Association and the American Telephone and Telegraph Company. It was the opinion of this committee that in view of improvements which had become possible in absolute measurements, electrical standards in the future should be based upon the absolute system of units. Proposals for the change were presented by the NBS to an Advisory Committee on Electricity established in 1927 by the International Committee and the 7th General Conference on Weights and Measures. The proposals were accepted and the 8th General Conference in 1933 definitely approved the principle of substituting the system of absolute electrical units for the international system. It delegated to the International Committee on Weights and Measures the power to fix

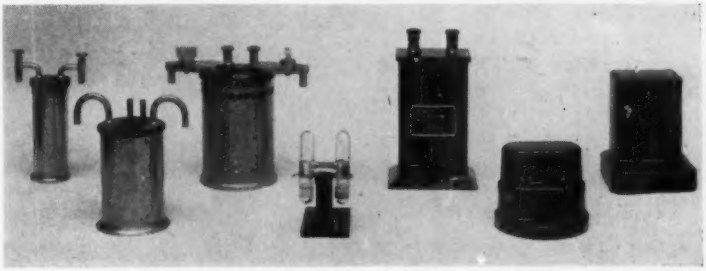

FIG. 4. Standard resistors and standard cells. The commercial types of standard cells are unsaturated but the standard at NBS is maintained by a group of 25 saturated cells like the unmounted cell in the center of the illustration.

the ratios between the corresponding units of the two systems and to set the date for the adoption of the new units. This was originally proposed for January 1, 1940. Obviously no international agreements were obtainable at that time but the project was definitely consummated as of January 1, 1948.

With the adoption of the absolute units it is still necessary to have concrete standards and these, as before, are wire resistors and standard cells, Fig. 4. It becomes necessary, therefore, to reassign to these standards new values in accordance with the absolute measurements made in the several countries on the basis of comparisons made at the International Bureau. The relations accepted by the International Committee on Weights and Measures at its meeting in Paris in October 1946 are as follows:

1 mean international ohm = 1.00049 absolute ohms
1 mean international volt = 1.00034 absolute volts.

The mean international units to which the above equations refer are averages of units as maintained in the national laboratories of 6 countries (France, Germany, Great Britain, Japan, USSR, and the United States) which took part in this work before the war. Naturally there were small

differences in the units as maintained by these several laboratories. Specifically, the standards as maintained at the National Bureau of Standards differed from these average units by a few parts in a million so the conversion factor for adjusting the values of standards in this country are as follows:

1 international ohm (U. S.) = 1.000495 absolute ohms
1 international volt (U. S.) = 1.00033 absolute volts.

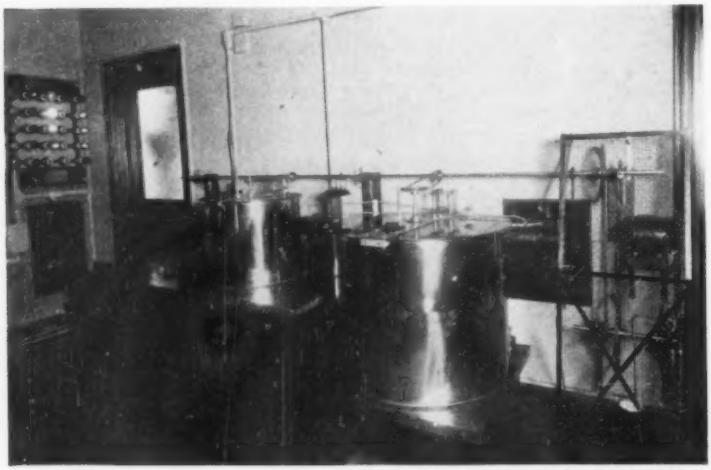

FIG. 5. Thermostatically controlled oil baths for standard cells at the National Bureau of Standards. The primary reference group is in the smaller bath at the left

With these as the basic units other NBS electrical units will be changed by amounts shown in the following tabulation:

1 international ampere = 0.999835 absolute ampere
1 international coulomb = 0.999835 absolute coulomb
1 international henry = 1.000495 absolute henries
1 international farad = 0.999505 absolute farad
1 international watt = 1.000165 absolute watts
1 international joule = 1.000165 absolute joules.

There is at present pending in Congress a Bill, designated as H.R. 4113 and S. 1850, to redefine the electrical units and establish the standards of electrical and photometric measurements. Section 2 of this Bill defines the ohm and section 3 the ampere in appropriate powers of ten based on the cgs system of electromagnetic units. The volt which is of particular importance to us at the present time is defined in Section 4 as follows:

> The unit of electromotive force and of electric potential shall be the volt, which is the electromotive force that, steadily applied to a conductor whose resistance is one ohm, will produce a current of one ampere.

This bill further provides that it shall be the duty of the National Bureau of Standards to establish the values of the primary electric and photometric

units in absolute measure and it repeals the Act of July 12, 1894, known as Public Law No. 105, 53rd Congress. This old law which has been on the statute books for more than 50 years was the outcome of the work of the International Committee which met in Chicago in 1893. There were some ambiguities in this law which were not recognized until years afterward and it is appropriate at this time to take the action contemplated by the new bill.

The National Bureau of Standards which has, since January 1, 1911, certified standards of electromotive force in terms of the international volt will from now on certify cells in terms of the absolute volt, named specifically the "volt." During 1947 such certificates have carried the additional information giving equivalent values in absolute volts corresponding to those certified in international volts. During 1948 the certificates will be made on the basis of the volt with the equivalent value in international volts. After 1948 it is believed that this reference to the older unit will no longer be necessary. The primary standard for the volt in this country consists of 25 saturated cadmium cells maintained at a constant temperature of 28°C. in the thermally controlled oil bath at the left in Fig. 5.

The fundamental electrochemical constant, the faraday, is measured in coulombs and does not involve electromotive force, but the change made in the electrical units involves the ampere also and therefore the value of the faraday. In discussing another paper (Trans. Electrochem. Soc. 90, 227 (1946) I indicated the value 96,487.9 absolute coulombs as the best absolute value which we can assign to this important constant. Experiments are now in progress for a redetermination of the faraday using new methods and apparatus and avoiding as far as possible the uncertainties of isotopic composition. From these experiments we hope to obtain a more accurate determination of the value of the faraday.

MANGANESE ACTIVATED CALCIUM SILICATE PHOSPHORS[1]

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ABSTRACT

Single activated $CaSiO_3 \cdot Mn$ phosphors absorb very little λ 2537 radiation and, consequently, do not fluoresce appreciably when so excited. Under cathode ray excitation the emission is strong and is made up of two bands, one peaking at 5600 Å, the other at 6200 Å, the longer of the two becoming more prominent at higher concentrations of MnO. Complete solid solution of larger amounts of MnO is made possible by firing the phosphors in atmospheres of steam and of hydrogen. Single activated $CaSiO_3 \cdot Pb$ phosphors produce blue or ultraviolet fluorescence, depending upon the conditions of preparation.

Double activated $CaSiO_3 \cdot Pb \cdot Mn$ phosphors, preferably prepared by steam firing, provide acceptable substitutes for ZnBeSilicate phosphors.

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They emit both visible light and useful ultraviolet when excited by λ 2537. Their sensitivity, efficiency, and color make them useful for application in fluorescent lamps. They show exceptionally bright second stage phosphorescence, and remarkable temperature stability.

In order to explain the mechanism of light production in double activated phosphors, internal optical excitation and paired Pb-Mn centers are ruled out, and a mechanism first proposed by Rothschild is tentatively accepted.

INTRODUCTION

Calcium silicate appeared to be an inviting base material for the study and development of new phosphors, particularly of materials which would be responsive to excitation by short ultraviolet energy. Many other simple silicates do respond to this excitation, and the strong cathode ray response of some calcium silicate phosphors indicates latent possibilities. Furthermore, calcium silicate is easy to synthesize, it is not affected by the nature of the atmosphere in which it is fired, and it may provide a link between typically crystalline phosphors and fluorescent glasses.

The present work, however, was also undertaken from a purely practical point of view. Its aim was to find an acceptable substitute for ZnBeSilicate phosphors such as are used in commercial fluorescent lamps, in case war or other contingencies should demand discontinuance of the use of beryllium compounds. This paper deals chiefly with work carried out several years ago which culminated in the development of calcium silicate phosphors double activated with lead and manganese as one such possible solution. In line with common notation, the phosphor will be referred to as $CaSiO_3$·Pb·Mn without any implications regarding molar proportions especially of the activators.

SINGLE ACTIVATED $CaSiO_3$ PHOSPHORS

A. $CaSiO_3$·Mn

In contrast to ZnO, calcium oxide can form true metasilicates of mol ratio 1:1 as well as orthosilicates of mol ratio 2:1. Phosphors may be prepared from either type of matrix, but the metasilicates fluoresce in general much brighter than the orthosilicates, at least at room temperature. Single activated phosphors have been known for some time.

Schloemer (1) appears to have been the first to mention a synthetic $CaSiO_3$·Mn phosphor; he found green and yellow cathodoluminescence associated with material fired as high as 1700°C. The intense yellow cathodoluminescence of Japanese wollastonite ($CaSiO_3$) (2) was related to the presence of small amounts of Mn (0.02 to 0.1%) in addition to a large number of other trace impurities. A synthetic product of substantially meta proportions, containing about 0.65% MnO and fired in air at 1250°C., is described as giving bright yellow cathodoluminescence (3). Gallup (4) found that the yellow fluorescing phosphors consisted of lath shaped crystals of the β or low temperature form of wollastonite. His Mn activated orthosilicates gave very weak red fluorescence when prepared in the high temperature α form. This is of interest in view of reverse findings for the metasilicate $CaSiO_3$, discussed below and in the following paper (5).

While the present work was in progress, Steadman (6) described two calcium silicate phosphors, one Mn activated, the other Pb activated, both

sensitive to cathode ray excitation. In order to obtain bright powders at reasonably low temperatures (1050°C.) he had to work with a 100% excess of silica over that required to form metasilicate.

None of the phosphors mentioned so far was credited with any noteworthy response to ultraviolet excitation. Powders of our preparation gave a brightness of the order of 10% or less, when compared with ZnBeSilicates of similar color.

The fluorescent color of $CaSiO_3$·Mn phosphors is quite generally described as "yellow." According to the present work, a much wider range of colors from light green to deep orange may be obtained if the phosphors are prepared properly. The color produced depends upon the amount of manganese which is actually incorporated in solid solution in the $CaSiO_3$ base. Very small amounts may be incorporated with ordinary long firing in air. Much larger amounts, such as several percent of MnO, were dissolved only when the phosphors were fired in special atmospheres such as steam, or in reducing gases such as hydrogen, or in their mixtures. The highest amount used in this work was 40 mol % MnO. For example, 1:1 molar mixtures of $CaCO_3$ and silica, containing several percent of Mn as carbonate, turned out brownish discolored and of weak fluorescence when fired in air at 1100°C. or higher, but they turned out bright fluorescent and perfectly white, indicating more complete reaction, when fired in steam as low as 1000°C. The brownish coloration was due to Mn_2O_3 which forms initially upon heating in air and which does not break down easily to give MnO (and $MnSiO_3$) when in contact with $CaSiO_3$. The reaction is much more sluggish than it is for Mn_2O_3 in contact with zinc silicate, in which case breakdown and solution occur much more readily (7). Steam catalyzes both the breakdown and the solution, while hydrogen serves chiefly as a reducing agent. The reduction of Mn_2O_3 with hydrogen stops at the stage of MnO; it does not go on to the free metal at the temperatures of interest.

The dependence of color upon manganese concentration is exemplified in Fig. 1 for three typical phosphors prepared by steam firing, and excited by cathode rays of low voltage and low current density at room temperature. It is apparent that the fluorescent emission is made up of two bands, one peaking in the green-yellow at about 5600 Å, and the other peaking in the orange at about 6200 Å. The green-yellow band is of sufficient intensity only at very low concentrations of MnO to be easily separated from the longer wavelength band produced by higher contents of MnO. Relative preponderance of the two bands, however, may also be associated with the crystal structure of the phosphors, as discussed in the following paper. Phosphors with very low content of MnO gave the α form of wollastonite, while phosphors with higher concentrations of MnO gave the β or low temperature form.

$CaSiO_3$·Mn phosphors exhibit rather strong phosphorescence after excitation with cathode rays. This does not appear to be due to secondary trace impurities.

As stated before, the phosphors do not respond appreciably to excitation by ultraviolet energy. The reason for this is the absence of a strong absorption band in the region 2000 to 4000 Å. This was ascertained by two experiments which, however, do not aim to take the place of exact crystal

measurements. Such measurements have been made by F. J. Studer of the G. E. Research Laboratory, and will be reported on separately.

In the first experiment, germicidal bulbs of Corning #9741 glass were coated with suspensions of quartz powder, unactivated $CaSiO_3$, and $CaSiO_3$·Mn phosphor, respectively, and regular lamps were made. The output of λ 2537 of these lamps should be a rough measure of the transparency (and

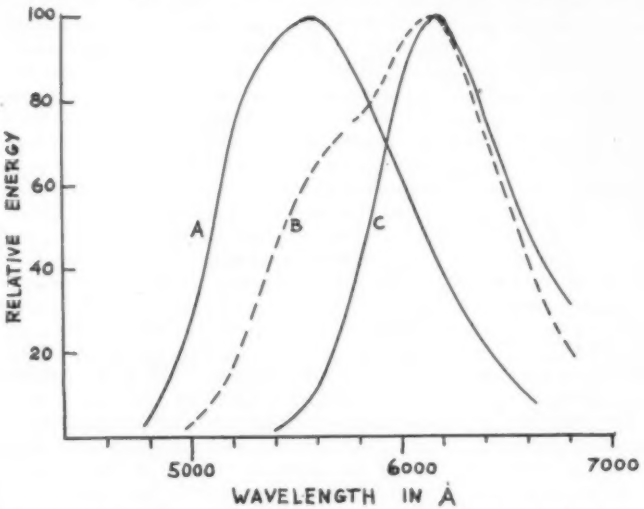

FIG. 1. Emission curves of steam fired $CaSiO_3$·Mn phosphors. A = 0.2% B = 1.0% C = 5.0% MnO.

scattering power) of the coatings. The lamps gave the following averaged outputs:

Lamp Coating	*Relative energy of 2537*
Quartz powder	14.0
$CaSiO_3$	9.1
$CaSiO_3$·Mn (1.8% MnO)	8.9

The test indicates that introduction of 1.8% MnO into the $CaSiO_3$ base did not add materially to its absorption in the short ultraviolet region. Some λ 2537 appears to have been absorbed by both materials, but probably dissipated as heat. The second experiment will be described in a later section.

While fairly transparent to λ 2537, $CaSiO_3$·Mn phosphors absorb shorter radiation such as λ 1849 more strongly. A lamp made with $CaSiO_3$·Mn phosphor gave 19% of the output of a standard lamp (after correction for the visible mercury light); measured as a dry powder with filtered λ 2537 radiation, the $CaSiO_3$·Mn phosphor gave only 12% brightness compared with the same standard powder. The difference of 7% appears to be due

to excitation by λ 1849 which is generated within the low pressure mercury discharge lamp.

B. $CaSiO_3 \cdot Pb$

Lead activated $CaSiO_3$ phosphors have been prepared by Fonda and by Steadman. Steadman's phosphor, again prepared with a 100% excess of silica and fired at 1050°C., is described as giving bright blue fluorescence under cathode ray excitation. Possible response to short ultraviolet, resulting in emission of long ultraviolet or visible light, was not indicated. Fonda's phosphor of true 1:1 composition and fired at 1100°C. or higher gave practically no visible light at all. It gave strong ultraviolet emission peaking near 3400 Å when excited by short wave ultraviolet (λ 2537), and a weak emission extending up to 4200 Å when excited by cathode rays. Some discussion of these materials and their emission curves are given in the Monograph of the Cornell Conference (1946), to appear in April, 1948. Additional work, now in progress, shows a characteristic dependence of emission upon firing conditions; this, too, will be reported on separately.

It would appear that Steadman's phosphor represents a material of transitional characteristics, for prolonged heating, or heating at higher temperatures, of corresponding powders prepared by us resulted in slowly decreasing efficiency of the blue fluorescence and corresponding increase of the ultraviolet emission.

Mechanical mixtures of the two phosphors individually activated with Mn and with Pb, show no unusual characteristics; they produce simply additive emission spectra. A mixture of $CaSiO_3 \cdot Mn$ and $CaSiO_3 \cdot SiO_2 \cdot Pb$ produces yellow and blue (blending to a "white") under cathode ray excitation, and some longer ultraviolet plus insignificant amounts of visible light when excited by λ 2537. A mixture containing Fonda's $CaSiO_3 \cdot Pb$ gives weak ultraviolet and bright yellow under cathode ray excitation, and strong ultraviolet plus insignificant amounts of visible light when excited by λ 2537.

Double activated $CaSiO_3 \cdot Pb \cdot Mn$ phosphor

When calcium silicate is prepared with both activators, lead and manganese present simultaneously, a new phosphor of different characteristics is obtained (8). The material fluoresces strongly when excited by λ 2537 radiation, emitting a bright band in the visible which is characteristic of Mn, and a weaker band in the ultraviolet characteristic of Pb. The peaks of these bands appear to be slightly shifted compared with the individual parent phosphors, and strong phosphorescence is observed after excitation with radiation shorter than 2500 Å such as λ 1849.

This phosphor represents one of the earliest examples of true double or sensitized activation.. The first case of similar nature was observed by Rothschild (9). More recent phosphors with sensitized activation include some interesting phosphates, such as calcium phosphate activated with Ce^{3+} and Mn (giving deep red radiation with λ 2537) (10), calcium apatites activated with Sb and Mn (giving a wide range of different colors with λ 2537) (11), and calcium carbonate activated with Pb and Mn (14).

Preparation of phosphor

The preparation of highly efficient phosphors, however, is not as simple as might be inferred from the above. Air fired mixtures prepared from

calcium, lead, and manganese carbonates again turned out brownish and of relatively low fluorescent brightness. The presence of lead in the mixture did not serve to catalyze breakdown and solution of Mn_2O_3. Fairly good products were obtained from pre-formed, white $CaSiO_3 \cdot Mn$ phosphors by adding the requisite amount of PbO or equivalent, and refiring at 1100 to 1200°C. Permanent or temporary fluxes did not prove helpful for the preparation of acceptable phosphors. The simplest method, giving generally the brightest powders, consisted again in firing an intimate mixture of all four components in an atmosphere of steam for about 2 hours at about 1150°C. If the phosphor did not turn out fully bright, it could be reheated until the optimum was reached, provided no impurities were introduced between fires, Fig. 2. Prolonged firing, on the other hand

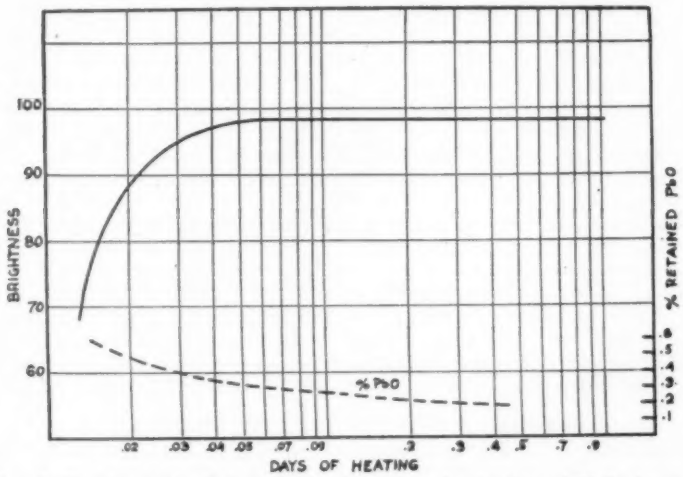

FIG. 2. Development of phosphor brightness, and retention of PbO, depending upon length of firing.

tended to promote particle growth. Some special atmospheres other than steam could also be used, although the powders fired in steam generally gave the brightest visible band and a weaker ultraviolet band, such as was desired.

Firing vessels of silica were most suitable even though their life was not too long. This was due to the strong devitrification action of the steam upon the fused silica. The latter, moreover, had to be heated above its normal devitrification temperature of about 1100°C.

Comparatively strong fluorescence was obtained even with a large number of different common and uncommon impurities present; this was surprising. Single activated phosphors are generally quite sensitive to foreign impurities not specifically added as activators. Double activated phosphors were expected to be much more so. As usual, however, the brightest powders were produced with raw materials of exceptional purity. In

particular, iron and sodium (alkali) caused a strong reduction of fluorescent brightness and ought to run well below 0.001% in the phosphor. Commercial calcium carbonates, the most convenient source of Ca, were found to be either not pure or not fine enough. Carbonate produced by a special process in the laboratory proved superior in all cases.

Not all of the lead introduced in the raw batch mixture was retained by the phosphors after firing. In fact, most of it volatilized out during the firing, whether in air or in steam, and regardless of the form in which the lead was introduced. For example, when pre-formed $PbSiO_3$ was used as a source of Pb, the volatilization was just as strong as with free PbO. This is also mentioned here as a note of caution for the preparation of the phosphor. The loss of PbO was quite rapid during the early stages of firing, and much slower thereafter. This is shown in Fig. 2 for one particular sample of $CaSiO_3 \cdot Pn \cdot Mn$ phosphor compounded to contain about 2% PbO, whose fluorescent brightness and retained lead content were followed over a prolonged period of heating.

The absolute amount of retained Pb was found to have little effect upon the brightness of the phosphors. A small though non-critical amount around 0.3% appears to be all that is necessary to produce a strong absorption band including λ 2537 which leads to fluorescence in the visible. For this reason the amount of PbO used in the raw batch mixture was not too critical, either. The optimum was found by trial as that amount which was not too large to cause sintering or fusion of the phosphor in firing, and not too small to be lost through volatilization before it was effectively combined with the silicate. Only one attempt was made to refire a phosphor sample with more PbO under pressure, in an effort to force more PbO into solution in the silicate. A noteworthy improvement in brightness was not observed.

The amount of retained PbO did not appear to be dependent upon the absolute MnO content of the phosphors.

Characteristics of $CaSiO_3 \cdot Pb \cdot Mn$ phosphors

Fig. 3 shows the emission curve for a typical, early phosphor with about 2.7% MnO such as may be used for the production of 6500° K daylight lamps. The curve was obtained from a lamp made with the phosphor coated on a bulb of ultraviolet transmitting glass (Corning #982) to permit escape and measurement of the ultraviolet emission of the phosphor. The energy values of the ultraviolet portion of the curve have been corrected for the partial absorption by the glass; absorption in the visible portion of the spectrum has not been taken into account. The data were obtained with a large quartz double monochromator, by B. T. Barnes of this laboratory.

The curve shows two distinct peaks, one in the ultraviolet region at about 3330 Å due to Pb, the other in the visible at 6100 Å due to Mn. Compared with individually activated phosphors, both peaks show a slight shift toward shorter wavelengths. However, this may be significant only with respect to the Pb band. The ultraviolet energy emitted by this sample was comparatively high; later preparations showed a lower emission and a corresponding increase in the energy of the emitted visible band. The ultraviolet emission is generally lower for phosphors with a higher

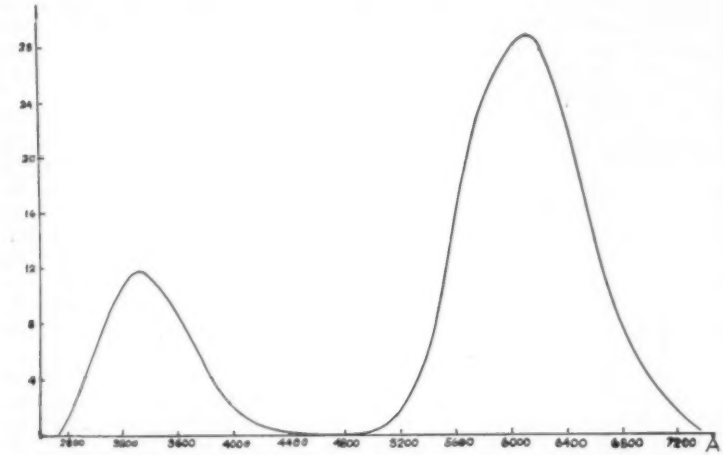

FIG. 3. Spectral energy emission curve of a typical $CaSiO_3$·Pb·Mn phosphor with approx. 2.7% MnO.

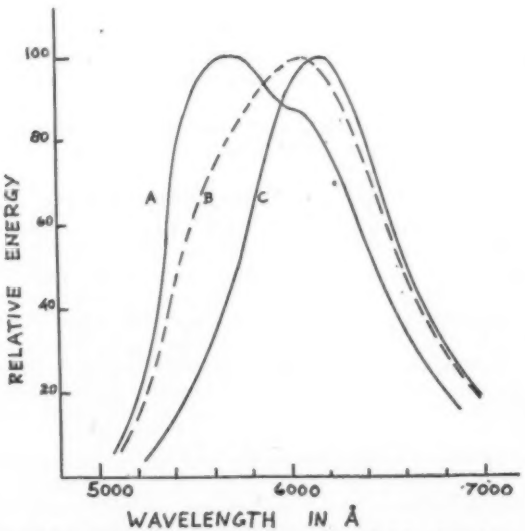

FIG. 4. Spectral energy emission of three $CaSiO_3$·Pb·Mn phosphors with increasing content of MnO. A = 0.2% MnO; B = 1.6% MnO; C = 5% MnO.

MnO content. Larger amounts of MnO also introduce a new absorption band in these phosphors, located in the 4000 Å region.

Dependence of the visible emission alone upon the manganese content is shown in Fig. 4 for phosphors with three different concentrations of MnO, and approximately the same content of retained PbO, all excited by λ 2537 radiation. Again the emission in the visible is made up of two bands the shorter of which is prominent only at low concentrations of MnO. The curves were obtained by F. J. Studer. Brightness of different phosphors as a function of the manganese content is shown in Fig. 5. The powders were excited with λ 2537 radiation and measured with G. E. photocells equipped with visibility correction and suitable red filters. Over a considerable range of concentrations the total brightness is nearly constant, but the red response increases due to the shift in relative intensity of the

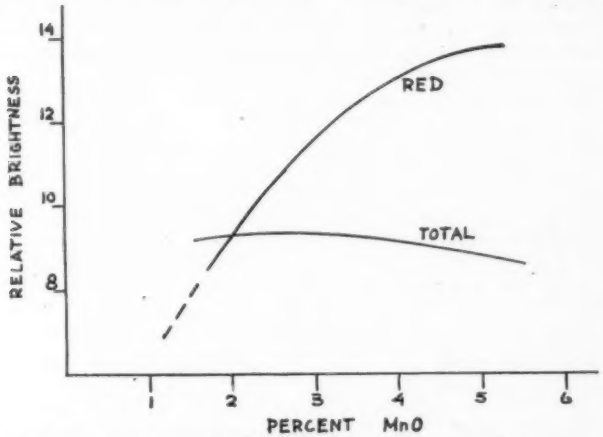

FIG. 5. Relative brightness of $CaSiO_3 \cdot Pb \cdot Mn$ phosphors with increasing content of MnO.

two Mn bands. The quantum efficiency of the phosphors was calculated to be better than 0.8.

These same phosphors, excited by cathode rays, yielded an emission spectrum of substantially the same character. The green-yellow component (5600 Å) of the emission band was more strongly excited by cathode rays than by ultraviolet, especially at high concentrations of MnO; this gave the cathode ray curves a slightly greater half-width. The Mn band in the double activated phosphors appeared to be quite the same as that of single activated phosphors with an equal content of MnO. The ultraviolet emission of the cathode ray excited, double activated phosphors was much lower in intensity than the same ultraviolet band excited by λ 2537. This paralleled the experience with single activated $CaSiO_3 \cdot Pb$ phosphors.

The ultraviolet emission of the $CaSiO_3 \cdot Pb \cdot Mn$ phosphors is of interest also from a practical point of view. A 40 watt fluorescent lamp made as described above can produce about 6000 *E* Vitons.[2] This is about 60% of

[2] 1 E Viton is defined as such an amount of radiant flux as will produce the same erythemal effect as 10 microwatts of radiant energy at λ2967.

the total erythemal ultraviolet produced, part of which is lost through absorption in the 982 glass. Thus the phosphors are unique in so far as they can be applied to provide illumination as well as healthful irradiation, without causing harmful erythema, if used in a lamp of the proper glass.

The ICI points of fluorescent lamps made with different calcium silicates roughly paralleled the line of points obtained with lamps coated with the redder varieties of ZnBeSilicate phosphors. However, they were somewhat closer to the blue locus of the ICI curve. Efficient samples of our preparation did not extend above the black body line toward the green. Thus "white" fluorescent lamps of high color temperatures could be produced with calcium silicate and magnesium tungstate phosphors alone, while lamps of lower color temperature required the addition of a third phosphor with higher green component. This latter phosphor could be chosen from the ZnBeSilicate or other systems, depending upon the spectral distribution

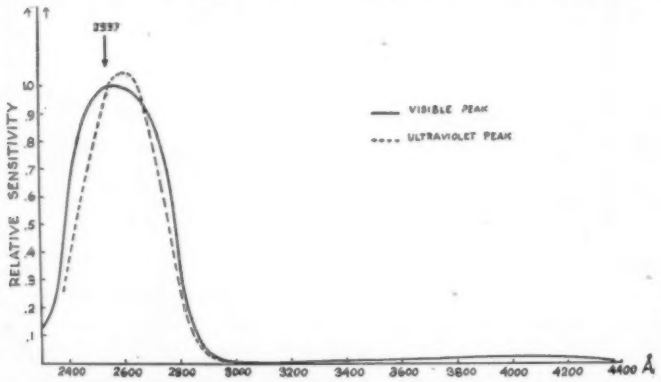

FIG. 6. Spectral sensitivity of $CaSiO_3 \cdot Pb \cdot Mn$ phosphors with respect to the visible and ultraviolet peaks.

and efficiency of the final "white" desired. The efficiency of lamps made with calcium silicate phosphors was not quite as high as with ZnBeSilicates, but acceptable, nevertheless. This is explainable, for the emitted ultraviolet energy is lost so far as direct utilization as visible light is concerned. The maintenance of the lamps was good.

Fig. 6 shows the spectral sensitivity of $CaSiO_3 \cdot Pb \cdot Mn$ phosphor with respect to both the visible and ultraviolet peaks. The response was at or very near the maximum for λ 2537 excitation, which makes it an efficient phosphor for use in F lamps. The sensitivity was found to be independent of the manganese concentration for the range up to 4% MnO studied. The data were again obtained by B. T. Barnes who used the radiation from a high pressure mercury lamp, refracted by the quartz double monochromator, to excite the phosphors. Although strongly responsive to cathode rays, the phosphors were not very well excited by the resonance and other radiation of the rare gases alone. Krypton and Xenon gave the best—yellow—colors of low brightness. All measurements were made at room temperature.

Another (qualitative) experiment served to demonstrate visually that the excitability of $CaSiO_3 \cdot Pb \cdot Mn$ phosphors is due chiefly to their ability to absorb λ 2537 radiation, as made possible by the secondary lead activator. A number of bulbs were coated with green zinc silicate phosphor. Over this layer, a second coating of the following materials was applied, each on individual bulbs: $CaSiO_3$ without activator; $CaSiO_3 \cdot Pb$; $CaSiO_3 \cdot Mn$; and finally, $CaSiO_3 \cdot Pb \cdot Mn$. If $CaSiO_3 \cdot Mn$ is transparent to λ 2537, then fluorescent lamps made from these double coated bulbs should be as green as the lamps with a coating of unactivated $CaSiO_3$. The lamps containing a coating of $CaSiO_3 \cdot Pb$ should show almost no visible green fluorescence except perhaps for what small amount could be excited by the longer ultraviolet radiation emitted by the $CaSiO_3 \cdot Pb$ phosphor. Finally, the lamps containing the coating of $CaSiO_3 \cdot Pb \cdot Mn$ phosphor should have about the same color and brightness as lamps containing this phosphor alone without any zinc silicate. The experiments fully confirmed the correctness of the assumptions, indicating complete absorption of λ 2537 by the double activated phosphor layer.

When excited by filtered λ 2537 radiation, the $CaSiO_3 \cdot Pb \cdot Mn$ phosphors exhibit a weak phosphorescence after an initial exponential decay, similar to ZnBeSilicates. Shorter ultraviolet, such as the λ 1849 radiation in a fluorescent lamp, produces a strong phosphorescence of yellow color, high brightness, and long persistence (second stage of bimolecular decay). Apparently the phosphor contains two types of traps, one of which is present in larger numbers and can be filled only after excitation with larger quanta such as λ 1849 (or cathode rays). A device to demonstrate the two types of phosphorescence separately has been described (12). The phosphor used in that device was the double activated $CaSiO_3 \cdot Pb \cdot Mn$ phosphor. Quantitative measurements of the decay curves, as made by G. R. Fonda, showed about the same shape as the curves for zinc silicate containing additional arsenic. The exponential decay of calcium silicate was somewhat slower than for zinc silicate. Phosphorescence was also observed for the ultraviolet emission band due to Pb.

The double activated phosphors are distinguished by a remarkable temperature stability, much better than that of ZnBeSilicates. At 430°C., for example, the fluorescent intensity of one sample with 5% MnO was still about 35% compared with the brightness at room temperature, according to measurements of F. J. Studer. As the temperature was increased, the fluorescent color became increasingly yellower. Measurements made to date give the appearance that this color shift involves the migration of a single band. However, judging from the experience with other phosphors, this does not appear to be very likely. A more plausible explanation might be that, through a peculiar coincidence, the relative intensity of the 5600 Å band increases, and the relative intensity of the 6200 Å band decreases, at the same uniform rate so as to simulate the migration of a single band. At the temperature of liquid air the fluorescence was very distinctly separated into the two characteristic bands with unchanged peak positions.

The phosphors turned out brightest with molar ratios of about 1:1 for $CaO:SiO_2$. Much higher percentages of silica offered no advantage so far as brightness and color of the powders was concerned. Orthosilicates with Ca_2SiO_4 as matrix gave only a weak response to excitation with λ 2537 or

with cathode rays at room temperature, whether they were fired in air or in steam. Products more basic than ortho did not fluoresce at room temperature.

Other secondary activators were also tried in place of lead but with not as much success. They absorbed the exciting energy of λ 2537 but did not pass it on to the Mn centers.

DISCUSSION

The visible Mn bands in the emission spectra of $CaSiO_3 \cdot Mn$ and $CaSiO_3 \cdot Pb \cdot Mn$ phosphors are practically identical, although considerably different quanta are required to excite the fluorescence to full strength. However, while absorption of λ 2537 by $CaSiO_3 \cdot Mn$ phosphors is weak, it is nevertheless present to some extent. Thus their efficiency with respect to the actually absorbed energy of λ 2537 may still be high. No exact data on absorption being available at this time, this question is left open.

A strong absorption band in the short ultraviolet region may be introduced in $CaSiO_3$ through incorporation of small amounts of other secondary activators. Although many elements will produce such an absorption band, not all of them can pass the absorbed energy on to the Mn centers in $CaSiO_3$ and thus free their latent excitability. Lead does it exceptionally well. This transfer of energy could occur directly between an excited Pb atom and a neighboring Mn atom, or by way of the matrix crystal. Direct coupling between Pb-Mn atom pairs was ruled out 1) because the number of Pb atoms in the phosphor is much smaller than the number of Mn atoms, and 2) because the brightness of phosphors with increasing MnO content did not depend upon the concentration of PbO beyond about 0.3%. For the range of 1 to 5% MnO, this amounts to, roughly, 10 to 50 Mn atoms for one atom of Pb. In spite of this disproportionate distribution, the efficiency under ultraviolet excitation is raised from about 10% for the single activated phosphor to about 80% for the double activated phosphor.

Simple radiative excitation by longer wavelength ultraviolet was ruled out on the basis of experiments described. No reason was seen why ultraviolet generated in the interior of a crystal should act differently than ultraviolet generated externally.

This left as third possibility to account for the transfer of energy the type of mechanism which was first suggested by Rothschild (8). This process assumed excitation of Mn atoms by a mechanism corresponding to collisions of the second kind, triggered by the excited Pb atoms and propagated by the atoms of the matrix crystal. This mechanism, leading to fluorescence of the Mn atoms in $CaSiO_3 \cdot Pb \cdot Mn$, is the reverse of a process, suggested by Curie and Saddy (13), leading to dissipation of energy by Fe or Co atoms in sulfide phosphors. In either case, energy from the primarily excited atoms is transferred indirectly to the other species of activator or impurity atoms. The latter may either utilize it for fluorescence or dissipate it as heat.

It will be apparent that our reasoning regarding a possible mechanism of light production in double activated phosphors had followed about the same lines of thought as were outlined clearly and in more detail in a very recent paper by Schulman et al. (14). For this reason it appeared unnecessary to present a more detailed discussion here again.

The double activation found for $CaSiO_3 \cdot Pb \cdot Mn$ phosphors is distinct from other cases where two or more activators combine to produce simply additive emission spectra without showing a change in phosphor sensitivity. Phosphors of the latter class include, for example, certain materials containing a rare earth in addition to other activators. For the sake of distinction, such phosphors might more appropriately be considered as examples of "dual" activation.

Various other connotations have been suggested all aiming to describe, with a single term, the mechanism of light production in double activated phosphors showing a change in sensitivity. These include, among others, sensitized, induced, auxiliary, cooperative, and double activation. Of these, the term "sensitized" as originally used by Rothschild has also been preferred by Schulman as most plausible. However, it does not appear to be a fully satisfactory choice, for a simple sensitizer ought not to introduce a rather strong emission band of its own. In the case of the calcium silicate phosphors, there was always found to be an emission band characteristic of Pb. This was also true for the other double activated phosphors mentioned before, except for $CaCO_3 \cdot Pb \cdot Mn$ for which data referring to possible emission in the ultraviolet were not given. It would be of considerable interest to search for such ultraviolet emission in this phosphor as well as in $NaCl \cdot Pb \cdot Mn$ (15). Since there was some evidence of unexplained mutual effects in $CaSiO_3$ phosphors, with Pb affecting the emission of Mn as well as Mn affecting the emission of Pb, the writer prefers to use the simple though less descriptive term of "double activation" for cases involving a change of sensitivity, at least until the mechanism of light production in these phosphors is better understood.

The writer wishes to express his thanks to B. T. Barnes, G. R. Fonda, and F. J. Studer for permission to use some of their data in this work.

Any discussion of this paper will appear in Volume 93 of the Transactions of the Society.

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THE STRUCTURE OF CALCIUM SILICATE PHOSPHORS[1]

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ABSTRACT

X-ray diffraction patterns were obtained for a variety of synthetic calcium silicate phosphors containing increasing amounts of lead monoxide, manganous oxide, or both, and fired in different atmospheres and at different temperatures. Powders with and without lead monoxide alone were found to give α or pseudowollastonite structure even when prepared as low as 1150°C.; powders containing manganous oxide, or lead monoxide and manganous oxide as activators showed increasing prominence of the low temperature β structure with increasing content of manganous oxide, even when fired considerably above the "normal" inversion temperature of 1200°C. The effect of steam in the preparation of the phosphors appears to be mostly catalytic with respect to rate of reaction and the development of more perfect crystals. The difference in fluorescent sensitivity between manganese activated phosphors with and without additional lead monoxide can not be explained on the basis of their (identical) lattice structure. The difference in light emission, however, might be correlated with the α and β structures respectively.

INTRODUCTION

The present investigation was undertaken for a dual purpose. Its first aim was to determine whether the crystal structure of $CaSiO_3 \cdot Pb \cdot Mn$ phosphors described in the preceding paper (1) could be identified with one of the three known modifications of $CaSiO_3$, or whether it represented a fourth and new form. The second aim was to find a correlation, if possible, between crystal structure and phosphor sensitivity to excitation by ultraviolet energy. It also seemed to be of particular interest to determine what significance if any, could be attributed to the action of steam upon the development of some particular crystal phase. It was pointed out in the preceding paper that steam provided an important aid for the preparation of $CaSiO_3 \cdot Pb \cdot Mn$ phosphors of high brightness.

THE STRUCTURE OF $CaSiO_3$

The lattice structure of "pure" calcium silicates including $CaSiO_3$ has been investigated extensively. The latter material occurs in nature as the mineral, wollastonite, of which certain varieties exhibit bright cathodoluminescence due to minor or trace impurities. $CaSiO_3$ occurs in a high temperature form, α wollastonite, also called pseudowollastonite, which is formed from the β or low temperature form when the latter is heated above the inversion temperature reported to be about 1200°C. Our own syn-

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thetic products prepared from very pure raw material at 1150°C. invariably showed the α or high temperature form. The change of phase proceeds quite rapidly. The reverse transformation, $\alpha \rightarrow \beta$, does not take place by simple cooling of highly heated α wollastonite; however, it may be catalyzed by the presence of foreign agents such as calcium fluoride or by excess of either of the components. Wollastonite is triclinic, while pseudowollastonite is monoclinic. In addition, Peacock (2) described a third, naturally occurring modification of wollastonite which is monoclinic and of volcanic origin in contrast to the more common triclinic form of sedimentary history. Peacock termed it "parawollastonite" and ascribed to it a stability range lying between that of β and α wollastonite.

From the published information and from a private communication by H. W. Rinn it may be gathered that the X-ray patterns of β wollastonite and of parawollastonite are quite similar; the intensities of the lines may vary somewhat but the angles should be the same. Thus diffraction patterns of the double activated phosphors might leave a choice between only two of the known forms of $CaSiO_3$.

STRUCTURE ANALYSIS OF $CaSiO_3$ PHOSPHORS

Crystallographic examination of the phosphors under a high power microscope did not lead to much success. The individual crystals were in the lowest micron range which was too small to allow positive identification of their habitus. It was also too small to differentiate between the β and the para forms.

X-ray diffraction patterns with molybdenum K_α radiation were taken of a great variety of samples several years ago when most of this work was carried on. More recently, renewed interest extended the study to patterns obtainable with the North American Philips Geiger counter X-ray spectrometer, which records the diffraction pattern resulting from copper K_α radiation. Comparison of the two methods showed that they are in virtually exact agreement. Many of the lines photographed were not as sharp as desirable but permitted accurate measurement nevertheless. This is due to the exceptional fineness of the powders studied, and to the low atomic number of the matrix ions. All patterns were taken by E. T. Asp of the General Electric Research Laboratory.

Patterns of the following compounds have been taken: $CaSiO_3$ without added activators; $CaSiO_3$ with increasing PbO content; $CaSiO_3$ with increasing MnO content; and $CaSiO_3 \cdot Pb \cdot Mn$ phosphors with varying amounts of both PbO and MnO. All powders were synthesized as described in the preceding paper, fired at various temperatures and in different atmospheres including air, steam, hydrogen, and others. In addition, the pattern of a good specimen of wollastonite mineral from California was taken, both as received and after heating to high temperatures.

Once the fundamental patterns had been worked out, the phosphors could be arranged in groups having either exclusively or at least predominantly the α or the β structure, respectively. In addition, some samples showed the most prominent diffraction lines of CaO and SiO_2, indicating incomplete reaction. This was especially true of the air fired materials. The steam fired products not only indicated nearly complete reaction in the two hours in which most samples were fired, but the lines

were also sharper and more intense, denoting better crystal formation. The steam fired samples, however, did not give any indication of a new $CaSiO_3$ phase.

The following tables contain, first, the principal lattice spacings (d-values) for a few materials having predominantly the α structure, second, the d-values for a few materials having characteristically the β structure, and finally, the structure of a variety of materials as selected from the group of all materials studied. The data of Tables I and II, were obtained

TABLE I. *Phosphors having predominantly pseudo* (α) *wollastonite structure*

Wollastonite H., R. and F.		2862 A $CaSiO_3$·Pb·1180°			2858 A $CaSiO_3$·Pb·(0.05) Mn			2856 A $CaSiO_3$·Pb·(0.20) Mn		
d	*I*	*d*	*I*	*Xtal*	*d*	*I*	*Xtal*	*d*	*I*	*Xtal*
		4.00	5	—	4.05	3	—			
								3.90	20	β
		3.80	5	α	3.77	7	α	3.72	17	α
								3.60	25	β
3.42	15	3.43	19	α	3.42	23	α	3.41	17	α
								3.31	17	β
3.23	100	3.25	100	α	3.23	100	α	3.18	100	α
								2.90	42	β
2.80	75	2.81	72	α	2.80	73	α	2.75	75	α
2.45	10	2.47	23	α	2.45	17	α	2.51	22	α
		2.35	5	α	2.35	5	α	2.41	25	$\alpha+\beta$
								2.26	12	β
								2.20	12	β
		2.16	3	α	2.16	7	α	2.16	13	α
		2.12	4	α	2.12	8	α	2.10	13	α
1.98	63	1.99	74	α	1.98	73	α	1.96	63	$\alpha+\beta$
								1.92	12	β
1.83	8	1.84	15	α	1.84	17	α	1.81	20	$\alpha+\beta$
1.69	3	1.70	13	α	1.71	7	α	1.70	17	α
								1.66	17	β
1.61	8	1.63	13	α	1.62	17	α	1.60	20	$\alpha+\beta$
1.54	3	1.54	8	α	1.54	5	α	1.55	8	α
1.476	8	1.48	15	α	1.48	20	α	1.46	13	α
1.400	5	1.400	6	α	1.400	10	α	1.400	8	α
1.293	3	1.300	5	α	1.300	10	α	1.290	8	α
1.250	8	1.251	13	α	1.250	11	α	1.249	8	α
		1.230	5	α	1.230	7	α			
1.180	3	1.182	4	α	1.182	7	α			

from the recorded spectrograms with copper radiation, on new and older preparations of samples. The data of Table III were obtained from the older patterns taken with molybdenum radiation.

The results for each phosphor are listed in three columns. Under the heading "*d*" are the lattice spacings corresponding to the lines of the patterns. They are the observed values in Å units. The error of recording is in some cases appreciable but there is no difficulty in arranging them in such horizontal columns that the values given in each line pertain to the lattice spacing between the same set of symmetry planes. Under the heading "*I*" are given the relative intensities as read from the recorded patterns but expressed as percentages of that specific spacing whose d-value

is most intense. The type of structure corresponding to a particular spacing, whether α or β, is given under the heading "Xtal."

The results of Table I are for three phosphors whose structure is predominantly in the α form. They contain 3% added PbO (only a fraction of this is retained in firing), plus 0, 0.05, and 0.20% manganese by weight. The structure of pure $CaSiO_3$, prepared at 1180°C. or even lower, was identical with the structure of the phosphor containing 3% added PbO.

TABLE II. *Phosphors having predominantly wollastonite (β) structure*

Wollastonite Ehrenberg		B120 $CaSiO_3$·750°			B49D $CaSiO_3$·Pb·(2.3)Mn			2842 A $CaSiO_3$·Pb·(1.0)Mn		
d	*I*	*d*	*I*	*Struct*	*d*	*I*	*Xtal*	*d*	*I*	*Xtal*
		3.95	19	β	4.00	19	β	4.20	18	
3.848	F	3.80	7	β	3.80	19	β	3.90	27	β
3.504	W	3.50	24	β	3.50	21	β	3.50	18	β
3.300	S	3.30	30	β	3.30	29	β	3.30	27	β
								3.25	46	α
3.097	M-W	3.09	19	β	3.08	16	β	3.09	14	β
2.976	vS	2.97	100	β	2.98	100	β	3.00	100	β
								2.82	41	α
2.786	W-F	2.80	10	β	2.80	13	β	2.80	18	β
2.714	W	2.71	9	β	2.70	11	β	2.73	6	β
2.570	F	2.55	5	β	2.55	6	β	2.55	9	β
2.468	W	2.50	29	β	2.46	26	β	2.50	18	β
2.351	M	2.35	24	β	2.33	16	β	2.35	18	β
2.294	M	2.29	25	β	2.28	8	β	2.28	18	β
2.188	vS-S	2.19	26	β	2.17	21	β	2.20	23	β
2.078	F	2.08	6	β	2.08	4	β	2.28	18	β
2.025	M-W	2.02	9	β	2.02	6	β	2.02	5	β
1.984	M-W	1.98	6	β	1.98	8	β	1.98	32	$\beta + \alpha$
1.888	W	1.91	5	β	1.91	5	β	1.91	5	β
								1.84	23	α
1.828	vS-S	1.82	16	β	1.82	13	β	1.80	6	β
1.757	W	1.74	6	β	1.74	12	β	1.76	11	β
1.720	vS	1.72	16	β	1.72	16	β	1.72	18	β
								1.62	14	α
1.606	vS-S	1.60	6	β	1.60	11	β	1.60	9	β
1.540	F	1.54	7	β	1.54	5	β			
1.477	S				1.475	11	β	1.480	18	β
1.364	S	1.370	6	β	1.360	5	β			
1.266	M				1.265	4	β			

For the sake of comparison, values are given in the first column for the $CaSiO_3$ tested by Hanawalt, Rinn, and Frevel (3). According to H. W. Rinn's communication, this material was synthesized at 1600°C. and is believed to be pure α wollastonite.

Two phosphors having predominantly the structure of the β form are grouped in Table II. This table also includes the results on a sample of pure synthetic $CaSiO_3$ prepared by firing in steam at 750°C. for sixteen hours. To establish the fact that its pattern is in fact that of the β form, comparison is made with *d*-values computed from the data of Ehrenberg (4) with copper K_α radiation. He tested a product prepared by firing $CaO + SiO_2$ at 1000°C., and also a particularly pure specimen of the nat-

ural mineral, wollastonite. The results from the two are virtually in exact agreement. In computing the *d*-values from his recorded angles, a weighted average of α_1 and α_2 was used for $\lambda = 1.5387$. The relative intensities of his lines are given by the symbols: S = strong, M = moderate, W = weak, F = faint, v = very.

The data of columns one and two are also in very good agreement with the pattern for a mineral sample of wollastonite from California, believed

TABLE III.

Sample	%MnO	%PbO (retained)	Atmosphere	T.	Structure
Wollastonite Mineral	—	—	As received		β
" "			Air	1210	α
" "			Steam	1150	β
B119 $CaSiO_3$ synthesized			Air	750	β
B120 " "			Steam	750	β
B101 " "			Air	1150	α + trace β
B102 " "			Steam	1150	α + trace β
B109 " "			Air	1240	α
B110 " "			Steam	1240	α
B91 " "	1.0	—	Air	1150	α + trace β
B93 " "	1.0	—	Steam	1150	β
B95 " "	1.0	—	H_2	1150	β
B97 " "	1.0	—	H_2 + steam	1150	β
B92 " "	5.0	—	Air	1150	α + trace β
B94 " "	5.0	—	Steam	1150	β
B96 " "	5.0	—	H_2	1150	β
B98 " "	5.0	—	H_2 + steam	1150	β
B24 " "	5.0	—	Steam	1150	β contracted
B26 " "	8.0	—	"	"	β "
AH139 " "	20 mol %	—	"	"	β "
AH140 " "	40 " "	—	"	"	β "
B88 " "	3.0	3.0	Steam	1150	β
B49A " "	0	0	Steam	1150	α + trace β
B49B " "	0	0.3	"	"	α + trace β
B49C " "	3.0	0	"	"	β
B49D " "	3.0	0.3	"	"	β

to be predominantly parawollastonite (β), as kindly communicated to us by H. W. Rinn.

In order to demonstrate the structures visually, the X-ray patterns as recorded for the various phosphors are reproduced in the photograph of Fig. 1.

Table III finally gives the structure analysis for a selected group of typical phosphors, prepared as indicated in the table, and tested with molybdenum radiation.

The data of the table show that the nature of the firing atmosphere has no effect upon the type of phase which develops; the latter is determined

only by the firing temperature and by the character of the activator metals. The firing atmosphere, however, does affect the sharpness of the pattern and the brightness of the phosphors, those fired in steam generally showing the greatest brightness, and the sharper, less diffused lines.

The table shows further that our synthetic $CaSiO_3$ powders, prepared at 1180°C. or even lower, gave the high temperature α structure, reported to be stable above 1200–1210°C. for mineral specimens. The α form per-

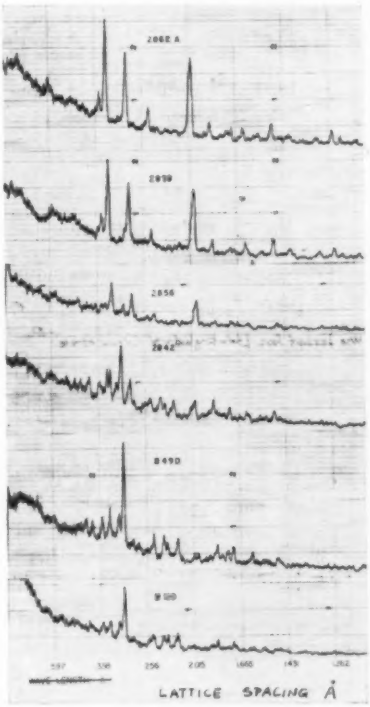

FIG. 1

sisted also with relatively small additions of PbO. Preparation of phosphors with much higher PbO content did not prove feasible at the high temperatures of interest, because most preparations either melted or sintered badly.

With manganese as activator, and either with or without added PbO, both structures may be obtained, depending upon the concentration of MnO. Certain small amounts are ineffectual, such as 0.1% manganese and less, so that the high temperature α form predominates in samples prepared at 1180°C. Somewhat larger amounts, from 0.2 to 0.5% manganese, cause the formation of considerable of the β form. At 1% manganese the

β form predominates, with only a small content of the α form. At 2.3% manganese, the β form is completely predominant, with no evidence of the α form.

Larger amounts of manganese do not change the crystal structure, but they do effect a contraction of the lattice spacings, as shown in Fig. 2. The

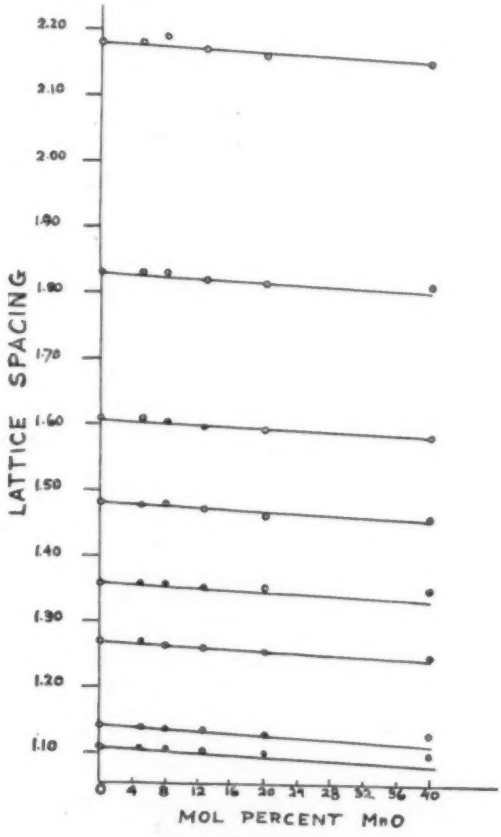

FIG. 2

extent of the contraction is roughly proportional to the manganese content. This is evidence that the manganese forms a silicate which enters into solid solution with the calcium silicate, at least up to 40 mole %, the highest concentration employed. The manganese ions presumably substitute for occasional calcium ions in the $CaSiO_3$ lattice, with a resulting slight reduction in spacing, for manganese has an ionic radius of only 0.91 Å compared with 1.06 A for calcium.

DISCUSSION

Synthetic preparations of $CaSiO_3$ showed the structure of the α form, even when prepared at temperatures as low as 1150°C. The literature lists 1200–1210°C. as values for the transition temperature of natural products. Our results with the mineral specimen in Table III are in accord with this. The apparent discrepancy might possibly be explained with Ostwald's step rule and with consideration of the kinetics of the $CaSiO_3$ formation. It appears that this material is not formed by direct synthesis from one mole CaO and one mole SiO_2. The primary reaction product is the orthosilicate, Ca_2SiO_4, from which the metasilicate is formed with the balance of SiO_2 in a secondary reaction of slower rate (5, 6, 7). Since the transformation $\alpha \rightarrow \beta$ does not take place on simple cooling, appearance of the α form might not be anomalous even when the material is synthesized as low as 1150°C. This would also hold true for phosphors synthesized with only PbO as activator.

The reason for the development of the β phase in phosphors containing appreciable MnO, or MnO and PbO, is not understood. The results, however, are in accord with those reported by Voos (8) who found that $CaSiO_3$ and $MnSiO_3$ can form a continuous series of solid solutions and that the $\beta \rightarrow \alpha$ inversion temperature of $CaSiO_3$ is considerably raised with increasing manganese concentration.

Phosphors containing MnO alone, or MnO and PbO, respectively, show identical crystal structure but different absorption and sensitivity to excitation by short ultraviolet. Air fired samples show the same structure as analogous steam fired samples, but considerably different intensity of fluorescence. Accordingly, the present work has shown 1) that the double activated $CaSiO_3 \cdot Pb \cdot Mn$ phosphors do not represent a new crystallographic form of calcium silicate, and 2) that there is no simple and direct relationship between the lattice structure and fluorescent sensitivity to ultraviolet radiation.

The emission of the phosphors containing manganese, however, may tentatively be correlated with structure as follows. As shown in the preceding paper, the emission is made up of two bands under both cathode ray and ultraviolet excitation. The shorter of these bands predominates at very low concentrations of manganese, and the longer one, at high concentrations. For intermediate contents of manganese, the emission is a mixture of both bands. It appears reasonable to associate the shorter wavelength band with the high temperature α form of $CaSiO_3$, and the longer wavelength band with the characteristic low temperature β form. This would have to be verified with preparations of pure α structure and high MnO content which, according to Voos, would have to be prepared at temperatures exceeding 1374°C.

The function of the steam in the preparation of the phosphors seems to be merely that of a nonpermanent gaseous catalyst which is desirable to promote reactivity and development of more perfect crystals. This may be accomplished through the formation of unstable intermediate hydrates or volatile silica. The catalytic effect would be stronger for the secondary reaction between Ca_2SiO_4 and SiO_2 leading to the end product $CaSiO_3$, than it would be for the primary reaction between CaO and SiO_2 which occurs very readily. Quite naively, one might even think of the steam

acting as a lubricant to provide better slippage for the atoms in diffusion to their proper places in the new lattice.

ACKNOWLEDGMENT

The authors wish to thank H. W. Rinn of the Dow Chemical Company for permission to use the information supplied privately. They also wish to express their sincere appreciation to E. T. Asp of the General Electric Research Laboratory in Schenectady who obtained all the diffraction patterns utilized for this work.

Any discussion of this paper will appear in the discussion section of Volume 93 of the Transactions of this Society.

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THE PRODUCTION OF BERYLLIUM[1]

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ABSTRACT

The production of beryllium metal by reducing beryllium fluoride with magnesium is described. Impure grades of beryllium oxide are dissolved in aqueous solutions containing ammonium bifluoride. The solution so formed is purified by a precipitation procedure, the precipitate separated by filtration, and the pure filtrate evaporated and crystallized to produce pure crystals of ammonium beryllium fluoride. These crystals are decomposed by heating into beryllium fluoride and ammonium fluoride which latter is recovered and returned to the process. Metallic beryllium is produced by heating the beryllium fluoride at temperatures below the melting point of beryllium with an amount of magnesium less than stoichiometrically required. The temperature is then raised to melt the beryllium which is recovered in the form of a solid plate after cooling. The beryllium fluoride content in the remaining magnesium fluoride slag is extracted with water and returned to the process. Data are given on analyses of the products involved.

INTRODUCTION

Metallic beryllium was first produced in 1828 by F. Wöhler (1) and A. A. B. Bussy (2) by reducing anhydrous beryllium chloride with potassium. The beryllium was obtained as a dark gray powder. The product

[1] Manuscript received January 12, 1948. This paper prepared for delivery at Columbus, Ohio Meeting, April 14–17, 1948.

probably was quite impure so that very few properties of beryllium could be determined.

The next advance in the production of beryllium occurred in 1898 when Paul Lebeau produced beryllium by electrolyzing sodium beryllium fluoride in a nickel crucible (3). He obtained the beryllium in small hexagonal crystals of sufficient size and quantity to determine several important properties of beryllium. Lebeau's work was investigated and followed by several workers, but a commercial method based on the electrolysis of sodium beryllium fluoride failed to develop due to the low yields obtained.

In 1928 a method for producing solid beryllium by electrolyzing fused basic beryllium fluoride in the presence of barium fluoride was developed by Stock and Goldschmidt (4). The electrolyzer consisted of a graphite crucible anode and a cylindrical water-cooled iron cathode. The temperature of the electrolyte was held above the melting point of beryllium. The iron cathode was barely immersed in the melt and continually raised, so that a cylindrically shaped lump of solid beryllium was produced. The fluorine released on the anode combined with carbon to carbon tetrafluoride. The life of the graphite crucible, therefore, was very short and the costs of the process were high.

The beryllium processes now in use are based on the production of pure beryllium halides from beryllium oxide from which the metal is produced either by electrolysis or by reduction of the halide with magnesium, calcium, or other metals with higher decomposition potentials than beryllium at the temperature and pressure employed in the reduction process. When a reducing metal is used, it is evident that this metal must be of high purity if a pure grade of beryllium is to be produced.

A process for electrolyzing beryllium chloride for the production of beryllium was patented by H. S. Cooper (5) in 1930. In this process a mixture of beryllium chloride and sodium chloride is melted in a stainless steel pot serving as the cathode. The anode consists of a graphite electrode. The temperature varies between approximately 730°C. and 820°C., depending on the beryllium chloride concentration in the melt. The flaky beryllium produced is deposited on the inner wall of the anode pot. The recovered flakes are cleaned by leaching with cold water, washing with alcohol, and drying at a low temperature to reduce surface oxidation. The dried product is compressed into briquettes and melted in a flux to produce pure solid beryllium metal.

The reduction of beryllium fluoride with magnesium has been studied by several workers and several patents (6) have been issued involving this principle. The methods described in these patents all have in common the reduction of beryllium fluoride in the presence of alkali or alkaline earth fluorides. These fluorides generally are added to produce low-melting magnesium-fluoride-containing slags to prevent a violent reaction. Carlo Adamoli (7) has claimed the decomposition of beryllium fluoride alone with stoichiometric proportions of magnesium, but prefers, according to his disclosure, to use additions of sodium fluoride.

This paper is a discussion of a process for reducing beryllium fluoride with a deficiency of magnesium without the addition of alkali or alkaline earth fluxes as developed by The Brush Beryllium Company (8) and includes a discussion of some technical problems connected with the commercial production of beryllium metal.

THE PRODUCTION OF BERYLLIUM FLUORIDE

Most of the present applications of beryllium require a metal of high purity. This necessitates the use of a beryllium fluoride of high purity and the processes for making it reflect this requirement. Several processes for the production of beryllium fluoride are described in the literature. Paul Lebeau (9) made the first pure beryllium fluoride by decomposing ammonium beryllium fluoride in 1898. L. Losano (10) produced pure beryllium fluoride by extracting impure grades of beryllium fluoride with alcohol. Another process in which beryllium oxide and ammonium bifluoride are heated in vacuum was patented by Carlo Adomali (11) in 1941.

The Brush Beryllium Company process described below is based on the Lebeau method of decomposing ammonium beryllium fluoride.

In the first step of this process impure beryllium oxide of low aluminum content is dissolved in a hot water solution of ammonium bifluoride or hydrofluoric acid, or a mixture of these. At the start, concentration of free hydrofluoric acid in the solution is adjusted to about 85 grams HF per liter. The dissolving tank is equipped with a stirrer and means of heating, such as steam-heated lead coils. Generally, a small excess of beryllium oxide is used to completely neutralize the hydrofluoric acid. The excess, being heavy, settles on the bottom of the dissolving tank and the solution of ammonium beryllium fluoride produced can be decanted readily through a small filter into a treating tank.

The clear beryllium oxide free solution obtained in this manner is treated with ammonium sulphide to precipitate all heavy metals. The precipitate formed is filtered off, washed with water and discarded. The clear filtrate is stored and analyzed for impurities and for its beryllium and ammonium content.

The process usually is carried out in such a way that there is less than the stoichiometric amount of ammonium fluoride in the filtrate to form the double fluoride. This deficiency is made up by adding a small amount of pure ammonium fluoride solution after the filtrate has been analyzed. After this adjustment, the solution which contains approximately 20 grams of beryllium per liter is evaporated and crystallized in a rubber lined vacuum evaporator. The crystals formed are continuously removed by the use of a stainless steel continuous centrifuge. Due to the high purity of the ammonium beryllium fluoride solution fed into the evaporator, the amount of mother liquor returned to the process is very small, generally 5% of the input. The ammonium beryllium fluoride crystals produced by this process are of high purity and usually show the following maximum amounts of impurities referred to the Be-content in the salt: 0.02% aluminum, 0.02% iron. The silicon content is not controlled as silicon is removed in the next step.

The equipment used in this process is lead or rubber coated, or is made of a resin-base material (such as Haveg) or stainless steel.

The ammonium beryllium fluoride crystals are decomposed into beryllium fluoride and ammonium fluoride by heating in graphite crucibles which may be heated electrically, preferably by high frequency induction, or by gas or oil. When gas or oil are used, the graphite crucible must be protected against oxidation by the flame with a refractory sleeve. The crucible is covered with a graphite lid which is cooled to prevent it from oxidizing.

The temperature of the graphite crucible walls is held at about 950°C. to obtain a high decomposition rate and to drive off the silicon present as silicon tetrafluoride. As the decomposition proceeds and the ammonium fluoride is driven off, additional amounts of the ammonium beryllium fluoride crystals are charged periodically into the crucible. By adding the crystals in small amounts at a time, excessive foaming is prevented and the maximum amount of molten beryllium fluoride is produced in the crucible before it is discharged.

The ammonium fluoride vapors are conducted from the top of the crucible to a cooled iron condenser where the ammonium fluoride sublimate is collected. The sublimate is approximately 70% ammonium fluoride and 30% ammonium bifluoride. The loss of ammonia is too small to justify recovery. The ammonium fluoride collected in the condenser is returned to the process, according to the flow sheet of Fig. 1. The molten beryllium fluoride is poured into a graphite container and solidified to a clear glass. Because this glassy product is not very hydroscopic it may be easily handled without absorbing appreciable amounts of moisture from the atmosphere. This product generally contains the following maximum amounts of impurities calculated on the Be-content of the beryllium fluoride: .02% aluminum, .02% iron, .01% silicon.

PRODUCTION OF BERYLLIUM METAL

Beryllium metal is produced by heating beryllium fluoride with pure magnesium or calcium, or a mixture of the two. Magnesium is generally preferred due to its lower cost. This reduction procedure had been studied by several workers and for some time the practical difficulties involved prevented this method from being commercially utilized. The difficulties were caused by the violence of the exothermic reduction reaction (12) and additional oxidation of magnesium caused by the presence of oxygen in the reaction vessel. The heat so produced, if permitted to heat the reaction materials above the boiling point of magnesium, may cause a sudden volatilization and increase in vapor pressure of the magnesium sufficient to cause material to be blown out of the reaction chamber. It is therefore desirable to carry out the reduction at the lowest possible temperature, or to control otherwise the reaction between the magnesium and the fluoride.

Beryllium fluoride is molten at about 900°C., and magnesium melts at about 650°C.; and the reaction products, beryllium metal and magnesium fluoride, both melt at considerably higher temperatures, 1250° to 1300°C. The reaction, therefore, which is carried out at temperatures close to the softening point of beryllium fluoride, produces solid materials forming hard crusts or layers in the reaction chamber. When the temperature is increased to melt the beryllium metal formed, these solid layers of reaction products soften and collapse as the temperature approaches the boiling point of magnesium. Any unreacted magnesium trapped in the shell of solid magnesium fluoride may therefore suddenly come in contact with overheated molten beryllium fluoride and a minor explosion may take place. These difficulties can be overcome by adding fluxes to the beryllium fluoride to lower substantially the melting point of the magnesium fluoride slag. This also serves to decrease the concentration of beryllium fluoride in the reaction mixture, thus tending to slow up the reaction and making it easier to handle in practice.

THE FUNCTION OF THE EXCESS BERYLLIUM FLUORIDE

In The Brush Beryllium Company process, the use of fluxes has been eliminated and instead an excess amount of beryllium fluoride is used in relation to the amount of magnesium. The use of excess beryllium fluoride had previously been tried by Robert Andre Gadeau (13), who came to the conclusion that this method is not practical because 1) the melting point of beryllium (1280°C.) lies above the boiling point of magnesium (1100°C.) and 2) beryllium fluoride is said to volatilize almost completely at the latter temperature.

Contrary to Gadeau, the process in which an excess amount of beryllium fluoride is used, as developed by The Brush Beryllium Company, has been found to be practical and adaptable for industrial use. One advantage of this process is that in making beryllium of high purity the control of the purity of fluxes is not required. The reaction is carried out in a graphite crucible held at a temperature of about 900°C. Crushed beryllium fluoride and magnesium in small pieces are charged in solid form at intervals in such a manner that the heat produced by the exothermic action is absorbed in heating and partially melting the excess beryllium fluoride. A violent reaction is thereby avoided and the reduction is carried out smoothly. The excess beryllium fluoride serves to produce a slag of magnesium fluoride and beryllium fluoride which has a low melting point compared to that of beryllium. This promotes the coalescence of the very small beryllium particles produced by the reduction reaction. The excess beryllium fluoride also dissolves any beryllium oxide present and this aids in coalescing the beryllium particles.

Another advantage of the excess beryllium fluoride is that the magnesium content in the beryllium metal formed may be reduced to a minimum because of a mass action that occurs. When the reaction mixture is finally heated to melt and coalesce the beryllium high frequency induction heating preferably is used so that contents of the graphite crucible are raised to a temperature of approximately 1300°C. At this temperature the beryllium fluoride-containing slag is very liquid and of such density that the molten beryllium metal floats on top of it. After this condition has been established, the heating is discontinued and the graphite crucible is cooled until the beryllium metal has solidified into a solid cake of beryllium which floats on top of the liquid slag. The cover of the graphite crucible is now removed and the solid beryllium plate formed is taken out with a pair of tongs. After the plate has been cooled down to room temperature, the slag adhering to its surface is removed either by leaching with water, or by sand blasting.

The liquid slag remaining in the crucible is poured out of the furnace crucible into a graphite pot. The beryllium fluoride content in the slag is subsequently recovered in the same process which is used for producing ammonium beryllium fluoride from beryllium oxide (see Fig. 1). The beryllium fluoride content is leached out by treating the slag with a hot slightly acid solution containing ammonium bifluoride or hydrofluoric acid. The acid is added to dissolve any beryllium oxide or small beryllium particles present in the slag. The beryllium fluoride itself dissolves easily in water. The magnesium fluoride remains unattacked in solid form and is separated in a small continuous centrifuge. The filtrate which contains

mostly beryllium fluoride is used to dissolve the ammonium fluoride sublimates recovered in the condenser attached to the beryllium fluoride furnaces (see Fig. 1). After this addition, the ammonium beryllium fluoride solution formed is purified in the same manner and simultaneously with the ammonium beryllium fluoride solution produced from beryllium oxide.

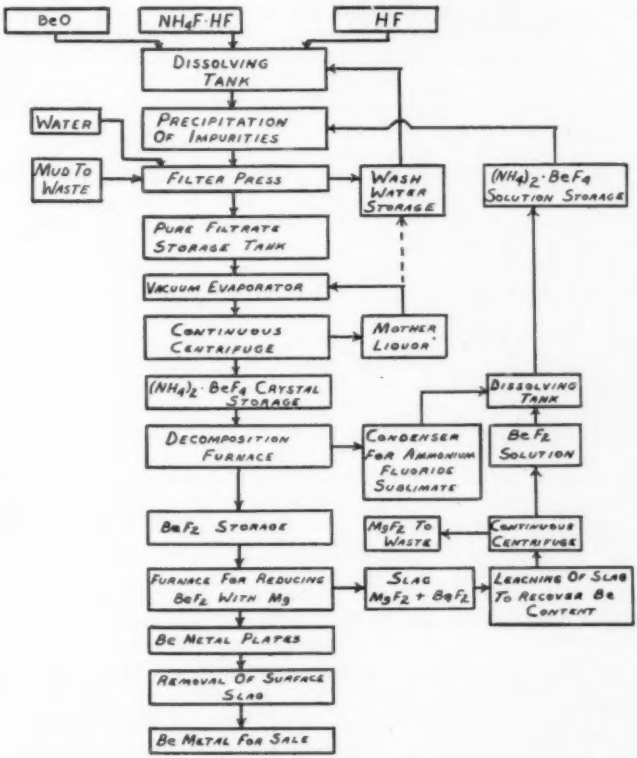

FIG. 1

PROPERTIES OF THE BERYLLIUM METAL PRODUCED

The solid beryllium metal plate formed by this process contains some slag in the form of small inclusions. The beryllium metal itself contains the following approximate maximum amounts of impurities in addition to small amounts of residual magnesium: 0.10% aluminum, 0.10% iron, 0.03% silicon, 0.05% copper, 0.05% manganese.

The virgin beryllium metal produced in this manner is suitable for alloying and for making castings of pure beryllium. The remelting of the

metal in making castings removes the slag inclusions. The metal is preferably remelted in vacuum. At atmospheric pressure fluxes with a high beryllium fluoride content are needed to protect the metal from oxidation. Both of these methods reduce the magnesium content in the metal so that finished cast beryllium contains less than 0.10%.

Of late there has been an increased interest in the health hazards associated with beryllium compounds and their applications. It is well to keep in mind that for many compounds of beryllium a low level of contamination of the atmosphere is essential to avoid pulmonary complications. The studies now being undertaken of the effects of beryllium compounds upon the respiratory system are sure to be illuminating and will go far toward making effective the control of the health hazard in the manufacture of beryllium and its compounds.

Any discussion of this paper will appear in the discussion section of Volume 93 of the Transactions of the Society.

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THE MECHANISM OF THE REDUCTION OF OXYGEN AT THE AIR ELECTRODE[1]

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ABSTRACT

Experiments are described which show that at all current densities the electromotive force of alkaline air-depolarizing electrodes is that thermodynamically required by equilibrium between oxygen and peroxide ion. In acidic solutions, however, the reduction of oxygen to hydrogen peroxide at carbon electrodes is irreversible. A tentative explanation for this is offered. In acidic and in alkaline air-depolarized cells hydrogen peroxide disappears by catalytic decomposition alone. The mechanism by which oxygen passes through air-depolarizing electrodes is shown to be diffusion, and a method for obtaining the diffusion coefficient is described.

INTRODUCTION

The physical properties of a commercial air-depolarizing carbon and the operation of an alkaline primary cell using this material have been discussed

[1] Manuscript received December 2, 1947. This paper prepared for delivery at the Columbus, Ohio Meeting, April 14–17, 1948.

by Heise and Schumacher (1). Nevertheless, the literature seems to contain no adequate discussion of the mechanism by which oxygen of the air travels through the electrode, nor of the kinetics of the reaction at the electrolyte-carbon-air interface. The present investigation was undertaken to study these points.

It was shown a long time ago (2) that at noble metal electrodes in dilute acid solutions oxygen is reduced to hydrogen peroxide with a current efficiency of 100% (or nearly so), but that the hydrogen peroxide so produced is decomposed by the electrode catalytically. This catalytic decomposition is exceedingly rapid at room temperature, which accounts for the low concentration of hydrogen peroxide usually found in such experiments. Fischer and Krönig (2) proved their point by working at very low temperatures and with other conditions set to minimize the catalysis. More recently W. G. Berl (3) has shown that in alkaline solutions, as well, oxygen is reduced solely to peroxide ion (HO_2^-) at activated carbon electrodes. Furthermore, he was able to prove that the measured electromotive force of a peroxide ion-oxygen couple was that predicted from independent themodynamic data. It thus seemed well established that 1) equilibrium can be obtained between oxygen and peroxide ions at certain carbon electrodes in basic solution, and 2) catalytic decomposition of hydrogen peroxide at carbon electrodes is likely to be rapid (4). It has been the purpose of the present authors to determine whether these principles could be applied in detail to a study of air-depolarizing electrodes upon discharge.

Six types of experiments have been performed: 1) Potentials of oxygen-peroxide couples at carbon and metal electrodes in alkaline and acid solutions have been measured. 2) The electrochemical reduction of hydrogen peroxide has been studied. 3) The rate of the spontaneous or catalytic decomposition of hydrogen peroxide has been determined under various conditions. 4) The rates of formation and decomposition of hydrogen peroxide in a discharging air-depolarized cell have been measured. 5) The transfer of oxygen through air-depolarizing electrodes has been studied. 6) Current-voltage curves for model air-depolarized cells have been obtained and interpreted. In all these experiments 5 molal sodium hydroxide and saturated ammonium chloride solutions were used as typical basic and acidic electrolytes, respectively, unless otherwise noted. The air-depolarizing electrodes used were manufactured for these experiments by the Primary Battery Division of Thomas A. Edison, Inc., at Bloomfield, New Jersey through the courtesy of L. S. Dunham, Chief Engineer.

1. Potentials of oxygen-peroxide couples under various conditions

The object of these experiments was to extend Berl's work (3) to acid media and to electrodes other than carbon. For the half cell reaction

$$OH^- + HO_2^- \rightleftharpoons O_2 + H_2O + 2e \qquad (1)$$

a change in electromotive force of 0.030 volts for a tenfold change in peroxide ion concentration at 25°C. is expected according to the Nernst equation

$$E = E^0_{HO_2^-} - \frac{RT}{2F} \ln \frac{P_{O_2}}{[OH^-]\,[HO_2^-]} \qquad (2)$$

$$E = E^0_{HO_2^-} - 0.0295 \log \frac{P_{O_2}}{[OH^-]\,[HO_2^-]} \qquad (3)$$

Berl confirmed this experimentally, obtaining an average value of 0.031 volts per tenfold change in peroxide ion concentration for a series of measurements in potassium hydroxide solutions of 0.1 to over 10 molar. Using a saturated calomel reference electrode, we measured the potential of an air-depolarizing electrode in 5 molal sodium hydroxide containing various concentrations of peroxide ion. A value of 0.034 volts for a tenfold change in peroxide ion concentration was obtained. It is felt that this is in adequate agreement with Berl's value as our measurements were not exceedingly refined. Replacement of the air-depolarizing carbon by porous sintered silver and nickel electrodes led, respectively, to values of 0.043 and zero for the change in voltage corresponding to a tenfold change in peroxide ion concentration. Apparently nickel is not sensitive electrochemically to the presence of hydrogen peroxide whereas silver and carbon are. Unfortunately, we were not able to test platinum electrodes.

The only conclusion which need be drawn, as far as the present paper is concerned, is that not all conducting materials can serve equally well as air-depolarizing electrodes, a specific catalytic or surface-active effect being required for the activation of oxygen. Berl (3) has postulated that the reduction of oxygen to peroxide ion takes place in two steps, as follows

$$O_2 + 2e \rightleftharpoons O_2^= \qquad (4)$$

$$O_2^= + H_2O \rightleftharpoons HO_2^- + OH^- \qquad (5)$$

Certainly the first step would be expected to have an appreciable activation energy and could, therefore, be subject to catalysis.

Similar potential measurements on an air-depolarizing electrode in saturated ammonium chloride solution gave zero for the change in voltage accompanying a tenfold change in hydrogen peroxide concentration. This inactivity of carbon in acid solutions seems at first surprising. The mechanism discussed just above should be no less applicable in acidic than in basic solutions. Thermodynamically speaking oxygen is as readily reduced in acid media as in basic (5). A possible explanation may be that hydrogen ions are strongly adsorbed by carbon and block off its active centers. There is certainly no doubt that carbon in the presence of oxygen will adsorb hydrogen ions from solution but not hydroxyls (6). Other differences in the behavior of carbon electrodes in acidic and in basic solutions will be noted in subsequent sections of this paper.

2. Electrochemical reduction of hydrogen peroxide

It is implicit from Berl's potential measurements (3) that hydrogen peroxide is not reduced to water at carbon electrodes in basic solutions. Wishing to test the reducibility of hydrogen peroxide directly in basic and acidic media, we simply passed a known current for a given length of time through solutions of hydrogen peroxide contained in a porous pot surrounding the cathode. Analyses for hydrogen peroxide were made on pipetted samples before and after passage of the current by titration with 0.1 N potassium permanganate in sulfuric acid solution. In the presence of chlorides the analysis was made by means of 0.1 N sodium thiosulfate after the peroxide had liberated iodine from an excess of potassium iodide (7). The values obtained were corrected for the quantity of peroxide decomposing spontaneously as measured in similar experiments in which

no current passed through the electrode. We found that in 5 molal sodium hydroxide solutions at graphite cathodes and at mercury cathodes with a current density of 0.01 amp./cm.^{2} no hydrogen peroxide was electrochemically reduced.

In saturated ammonium chloride, however, a considerable amount could be reduced at the same current density at graphite cathodes. Thus, we again find a difference in the behavior of hydrogen peroxide in ammonium chloride and in sodium hydroxide solutions, and again the reason is not obvious. We are at present no more able to say why hydrogen peroxide is easily reduced in acidic but not in basic media than we were able to say why oxygen is reversibly reduced in basic but not in acidic media (Sec. 1). According to thermodynamic data (5) there is very little difference in the potentials for the reduction of oxygen to hydrogen peroxide in acidic and basic media, nor is there a great difference in the corresponding potentials for the reduction of hydrogen peroxide to water. Hence, it is believed that a precise knowledge of the kinetics involved is necessary for explaining the two differences.

When an air-depolarizing electrode was substituted for the graphite, the hydrogen peroxide was no longer reduced in ammonium chloride solution. Thus, when hydrogen peroxide and oxygen both compete for electrons the rate of reduction of the latter is much greater than that of the former. In a functioning air-depolarized cell it seems likely, therefore, that hydrogen peroxide is lost by catalytic decomposition only.

3. Spontaneous decomposition of hydrogen peroxide

It is well known that hydrogen peroxide is relatively stable in acidic solutions but decomposes rapidly in basic solutions (8). The decomposition can be catalyzed in either case, and usually appears to be a first order reaction (8). The present investigation required some data on the rate of decomposition under the conditions prevailing in air-depolarized cells. To beakers containing 100 cc. of electrolyte, a suitable amount of hydrogen peroxide was added. The samples were then allowed to stand at room temperature—close to 25°C.—portions being withdrawn for analysis (as in Sec. 2) at appropriate intervals of time. The results are plotted in Fig. 1. In most cases duplicate runs were made showing good agreement.

Reference to Fig. 1 will disclose that all of the systems investigated seem to have first order rate constants. The rate constant is calculated as follows. According to the definition of a first order reaction

$$\frac{d[N]}{dt} = -k[N] \tag{6}$$

where [N] is the concentration of the decomposing material (moles per liter), k is the first order rate constant, and t is time (in seconds). Integrating the above expression and substituting common logarithms we obtain

$$\log [N] = \frac{-k}{2.303} t + C \tag{7}$$

where C is a constant. Thus, the slope of log [N] versus time yields k, the unit of which is reciprocal seconds.

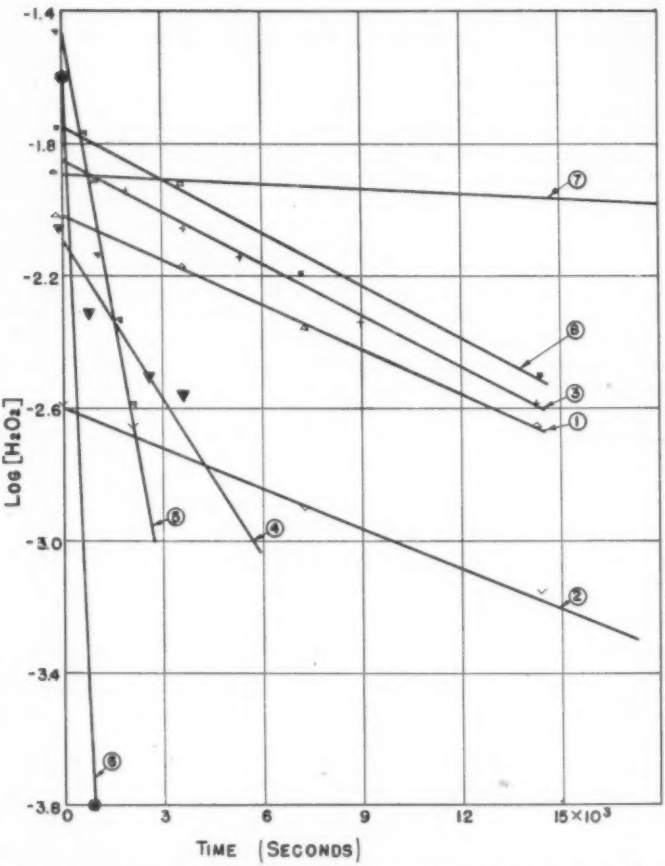

FIG. 1. Rate of decomposition of peroxide; (1) and (2) with 5 molal NaOH, (3) 0.5 molal NaOH, (4) and (5) 5 molal NaOH plus carbon, (6) 5 molal NaOH plus cuprate ion, (7) saturated NH_4Cl, (8) sat. NH_4Cl plus carbon.

TABLE I.—*Rate of decomposition of hydrogen peroxide*

Experiment No.	k (sec.$^{-1}$)	Electrolyte
1	1.07×10^{-4}	5 molal NaOH
2	0.97×10^{-4}	5 molal NaOH
3	1.18×10^{-4}	0.5 molal NaOH
4	3.7×10^{-4}	5 molal NaOH + carbon
5	$12. \times 10^{-4}$	5 molal NaOH + carbon
6	$50. \times 10^{-4}$	5 molal NaOH + trace of $CuSO_4$
7	$.05 \times 10^{-4}$	saturated NH_4Cl
8	1.2×10^{-4}	saturated NH_4Cl + carbon

In Table I the values of k and the conditions of the experiment are listed for each plot in Fig. 1. Experiments 1 and 2 show that the rate of decomposition of peroxide is first order over a wide range in peroxide concentration, while expt. 3 shows that the rate is not affected by hydroxyl ion concentration as long as peroxide ions are actually present. In expts. 4 and 5 increasing portions of ground, unwaterproofed air-depolarizing carbon were added. These data are somewhat less accurate than those of the preceding experiments but it is clear that carbon catalyzes the decomposition of peroxide ion strongly. From expt. 6 we gather that cuprate ion ($CuO_2^=$) is a more active catalyst than carbon. Expts. 7 and 8 prove that the rate of decomposition is comparatively slow in acid media but that again the reaction can be catalyzed by carbon.

Two general conclusions should be drawn from these experiments. First in studying an air-depolarized cell in operation we now can set a lower limit to the rate of decomposition of hydrogen peroxide—that found for 5 molal sodium hydroxide. The actual rate at the carbon electrode is undoubtedly faster, but just how much faster we do not know. In Sec. 4 this topic will be pursued further.

Secondly we found, as have others (8), that hydrogen peroxide is much more stable than peroxide ion towards spontaneous decomposition. One should remember that, on the other hand, it was the free acid which was more easily reduced electrochemically (Sec. 2). Therefore, it is important once again to consider the particular reaction mechanisms involved. As far as we know there is at present little or no data on the reduction of hydrogen peroxide, and while there is a great deal of data on the catalytic decomposition of hydrogen peroxide it is not too well understood (8).

4. Production and decomposition of peroxide in a functioning air-depolarized cell

The main object of these experiments was to determine the rate at which peroxide is actually decomposed in an air-depolarized cell as it is being discharged at various current densities. According to Faraday's laws:

$$\frac{dN}{dt} = \frac{I}{nF} \tag{8}$$

where dN is the number of moles of hydrogen peroxide produced in time dt (seconds), I is the current (amperes), n is the number of electrons required to produce one molecule of hydrogen peroxide from oxygen, and F is the Faraday (96,500 coulombs). In terms of concentrations

$$\frac{d[N]}{dt} = \frac{I}{2Fv} \tag{9}$$

where v is the volume of the electrolyte in liters and the other quantities are as previously defined. According to the results of Sec. 3, the rate of decomposition of peroxide is given by equation 6. Since the processes of formation and decomposition go on simultaneously we can write as the resultant rate of reaction

$$\frac{d[N]}{dt} = \frac{I}{2Fv} - k[N] . \tag{10}$$

At equilibrium the rate becomes zero, hence

$$\frac{I}{2Fv} = k[N] \tag{11}$$

assuming that I and k are constant with respect to time. If our various assumptions are correct then we should find that 1) [N], the concentration of peroxide, becomes constant after a certain length of time; 2) for different current densities a constant value of k is obtained from the corresponding equilibrium concentration of peroxide, [N], in equation 9 and this value is greater than the minimum mentioned in Sec. 3, next to the last paragraph

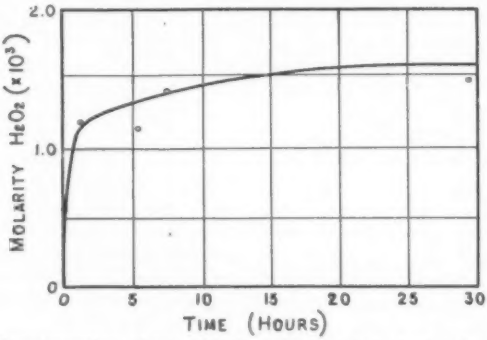

FIG. 2. Concentration of peroxide in a discharging air-depolarized cell

TABLE II.—*Rate of decomposition of peroxide ion in a discharging Air-Depolarized Cell*

Current Density (ma./cm.²)	Concentration HO_2^- (moles/liter)	Rate Constant, k (sec.$^{-1}$)
0.33	1.77×10^{-4}	29×10^{-4}
3.9	2.14×10^{-3}	28×10^{-4}
6.2	3.98×10^{-3}	24×10^{-4}
13.8	1.15×10^{-2}	19×10^{-4}
14.2	6.46×10^{-3}	34×10^{-4}

The experiments were performed using model air-depolarized cells consisting of 50 cc. of electrolyte (5 molal NaOH), zinc electrodes, and air-depolarizing electrodes of 15 cm.² surface area exposed to the electrolyte. These cells were discharged through suitable resistances and samples of the electrolyte were periodically removed and analyzed in the manner previously described. A typical set of data are plotted in Fig. 2, from which we see that the concentration approaches a limit slowly, as predicted above, but that the points are somewhat scattered. In a few cases the concentration actually decreased somewhat after a very long time. It is believed that this occurred only after the solution became nearly saturated with zinc, and is not pertinent to the present discussion. In Table II there is listed the equilibrium concentration of peroxide (molarity), current density (milliamperes per square centimeter of the exposed air-depolarizing electrode

surface), and k (sec.$^{-1}$) calculated according to equation 11. Each set of data here represents a separate experiment similar to that plotted in Fig. 2. Although the values of k vary from 19 to 34 $\times$ 10^{-4} sec.$^{-1}$ the amount of scatter is not surprising since we are dealing with catalysis in an unknown volume of carbon. The active volume is proportional to the outer surface, which we can measure; but it is also proportional to the depth of "wetting" by penetration of the electrolyte, which is immeasurably small and which may also be different in different experiments.

As predicted above the average value of k = 27 $\times$ 10^{-4} sec.$^{-1}$ is greater than that obtained independently in Sec. 3 for the specific rate of decomposition in 5 molal NaOH, which was k = 1 $\times$ 10^{-4} sec.$^{-1}$. Since peroxide is decomposed more rapidly at the surface of the carbon electrode than in the bulk of the solution, it is probable that the concentration at that surface is less than in the solution. In Sec. 6 we shall return to this question.

A similar group of experiments was attempted with saturated ammonium chloride as the electrolyte. Unfortunately equilibrium could not be obtained in these experiments before destruction of the carbon surface took place by precipitation on it of crystals, presumably of $ZnCl_2 \cdot 2NH_3$. We estimate, however, that in ammonium chloride the corresponding value of k = 15 to 20 $\times$ 10^{-4} sec.$^{-1}$.

5. Transfer of oxygen through air-depolarizing electrodes

We proceed now to the very important question of how oxygen reaches the electrolyte interface through a porous carbon. Since there is normally no pressure gradient across an air-depolarizing electrode the process of transfer must be diffusion rather than convection. In diffusion of one gas through another the total pressure is everywhere the same and where the concentration of one gas decreases that of the other increases just enough to compensate. To such a system Fick's Law for linear diffusion applies,

$$\frac{ds}{dt} = DA\frac{dc}{dx} \tag{12}$$

where ds is the amount of material crossing a boundary of cross section A in the time dt when the concentration gradient is dc/dx. D is the diffusion coefficient, whose units are commonly cm.^{2}/sec. Fick's equation can easily be evaluated for a rectangular block of constant cross section A and length x, when the concentrations C_1 and C_2 at either end remain respectively constant, giving

$$\frac{ds}{dt} = \frac{AD(C_2 - C_1)}{x}. \tag{13}$$

The experimental conditions are realized by coating the sides of a rectangular block of porous carbon, so that diffusion can take place only in the vertical direction. The lower end of the block is then immersed in a 5 molal sodium hydroxide or a saturated ammonium chloride solution and the electrode is shorted through an ammeter to a zinc electrode large enough to insure that the current will not be limited by anodic polarization. From the current obtained (after the cell comes to equilibrium) and Faraday's laws we obtain $\frac{ds}{dt}$, the oxygen transported in moles per

second. In this calculation it is assumed that the oxygen given off by the decomposing hydrogen peroxide is all available for further reduction, or in other words

$$\frac{ds}{dt} = \frac{I}{4F}. \tag{14}$$

C_2, the concentration of oxygen above the electrode, remains constant at its usual value of 8.6×10^{-6} moles/cm.^{3}. At the lower surface of the electrode the concentration of oxygen, C_1, is assumed in this case to be zero, since molecules of oxygen are being used up as fast as they arrive, our experiments having been set up so that their rate of arrival is the limiting factor. If our assumptions are valid, substitution in equation 13 should lead to a rational figure for D, independent of the length and cross section of the electrode. Table III gives the calculated diffusion coefficients for three carbons of different sizes in sodium hydroxide and one in ammonium chloride. All experiments were carried out at approximately 25°C. The four values for D are seen to be within the limits of error in measuring the dimensions of the blocks.

TABLE III.—*Rate of diffusion of oxygen through Air-Depolarizing Electrodes*

Length of block (cm.)	Cross Sectional Area of block (cm.^{2})	Equilibrium current (amp.)	Diffusion Coefficient (cm.^{2}/sec.)
8.4	14.2	0.386*	0.0687
7.6	1.56	0.047*	0.0680
3.15	1.58	0.116*	0.0696
8.65	15.1	0.388†	0.0670

* Cell with 5 molal NaOH as electrolyte.
† Cell with saturated ammonium chloride as electrolyte.

It is of interest to compare our figure for D, 0.068 cm.^{2}/sec., with similar diffusion coefficients given in the literature. Penman (9) reports measuring the rate of diffusion of carbon disulfide vapor, acetone vapor, and carbon dioxide through soils and other loose powders of varying porosities. He found that for all three gases diffusing through air in all the materials investigated (which did not include porous carbons) there was for any given gas a common expression connecting Do, its diffusion coefficient in free air, D, its diffusion coefficient in the given medium, and P, the porosity of the medium, as follows

$$\frac{D}{DoP} = 0.66. \tag{15}$$

The constant value of 0.66 held for porosities from nearly zero to 0.7. To apply this equation to oxygen in our porous carbon we need figures for Do and P. The diffusion coefficient, Do, for oxygen in air (10) at 25°C. is 0.206 cm.^{2}/sec. The porosity of the air-depolarizing electrodes was determined by impregnating a weighed block of known volume with carbon tetrachloride and reweighing. The volume of the carbon tetrachloride divided by the volume of the block gives the fraction porosity. A value

of 0.56 was obtained. Substitution in the expression D/DoP yields a ratio of 0.59, some ten percent lower than that reported by Penman. We are not able to say at present whether the discrepancy is due to a real difference between porous carbons and Penman's loose particles, or whether some of our assumptions were not strictly true.

In the experimental determination of D the conditions were so chosen that C_2, the concentration of oxygen at the electrolyte interface, was zero. This was done because we know of no practical way to measure the oxygen concentration directly at that point in a discharging cell. Fick's Law (equation 13) however, applies to all cases where C_2 and C_1 are respectively constant. Since we now know the magnitude of D we can predict C_2 for any corresponding equilibrium current. In Sec. 6 we shall use this relationship.

If pure oxygen at one atmosphere pressure rather than air is fed to an air depolarizing electrode which has been purged of its nitrogen, a very high current drain can be maintained when the electrode is shorted to a zinc electrode. In one experiment the amperage with pure oxygen was twelve times that with air. It is not known precisely what limited the current in the experiments with oxygen. It is interesting to note, however, that the electrolyte crept into the electrode fairly rapidly—one centimeter per day rather than the usual 2 millimeters per year (1). We believe that in this case the mechanism is bulk flow of oxygen rather than diffusion. In the complete absence of nitrogen or other inert gas a pressure gradient can exist within the carbon if oxygen is being consumed at the lower end. Because of this low pressure in the region of oxygen consumption, the electrolyte is sucked into the porous carbon. Thus, we see that the nitrogen of the air is actually useful in the operation of air-depolarizing electrodes.

6. Current-voltage curves

The final experiments were concerned with measuring the terminal voltage of an air-depolarized cell as a function of current density at the carbon electrode. Model air-depolarized cells were set up just as in Sec. 5 except that here a variable resistance was put in series with the ammeter and a voltmeter was placed across the cell. Calibrated Westinghouse instruments were used and the ammeter readings were corrected for the current flowing through the parallel voltmeter. Various resistances were chosen and for each the corresponding voltage and current were read periodically until they became constant. The attainment of this equilibrium required from 10 to 60 minutes for each pair of readings. The object of these experiments was to ascertain whether the electromotive force developed by an air-depolarized cell at all current densities is that required by equilibrium between oxygen and hydrogen peroxide. In general one can measure the potential of a discharging electrode by pressing the outlet of a calomel half cell close to it (11) and switching off the polarizing current just before the potential versus calomel is read. Unfortunately, the method fails with air-depolarizing electrodes since there is apparently a barrier of high resistance at all gas electrodes (11). It was necessary, therefore, to use an indirect method for getting at the unknown potential.

The voltage, V, delivered by a discharging cell is given by

$$V = E - IR_i \tag{16}$$

where E is the electromotive force of the cell, I is the electric current it is passing, and R_i is its internal resistance. The electromotive force, E, is equal to the algebraic sum of the potentials of the zinc and of the oxygen electrode

$$E = E_{Zn^{++}} - E_{HO_2^-} \tag{17}$$

which becomes, upon substitution of the Nernst equation (our equation 2),

$$E = E_{Zn^{++}} - E^0_{HO_2^-} + \frac{RT}{nF} \ln \frac{P_{O_2}}{[OH^-][HO_2^-]} . \tag{18}$$

This equation provides the required indirect method of evaluating E at any given current, for the three terms on the right-hand side can be measured or calculated.

In our experiments $E_{Zn^{++}}$, the potential of the zinc electrode, was measured versus a saturated calomel electrode for each value of I.

The term $E^0_{HO_2^-}$ is given by Latimer (5) as +0.076 volts.

The pressure of oxygen at the electrolyte-air-carbon interface, P_{O_2}, is obtained by the application of Fick's Law as outlined in Sec. 5. Since electrodes with coated sides were used in all these experiments, the relationships there derived are applicable. Combining equations 13 and 14, and recalling that for a perfect gas

$$C = \frac{P}{RT} \tag{19}$$

(where C is the concentration in moles/cm.^{3}, P is the pressure in atmospheres, and R is the gas constant expressed as cm.^{3}-atmospheres per °K) we obtain

$$P_{O_2} = 0.21 - \frac{IxRT}{4FAD} \tag{20}$$

The concentration of peroxide ion is calculated by the method outlined in Sec. 4, using equation 11

$$[H_2O_2] = \frac{I}{2Fkv}$$

with a value of $k = 27 \times 10^{-4}$ sec.$^{-1}$.

As previously mentioned this expression yields the concentration of peroxide in the bulk of the electrolyte, whereas the actual concentration at the surface of an air-depolarizing electrode may be much smaller. It is not known at this time how to calculate the concentration at the electrode. One should note, however, that if the concentration of peroxide at the electrode is, for example, one hundred fold smaller than assumed, the calculated potential will be only 0.06 volts lower than the true potential.

The final factor of equation 18 which must be evaluated is the hydroxyl ion concentration, which was initially 5 molal. As the cell discharged and zinc went into solution some hydroxyl ion was, of course, used to form the zincate complex. Analysis of our most concentrated zincate solution showed that the amount of hydroxyl used up was never significant, causing

at most an error of about 0.001 v. at the greatest current density. Moreover, the Nernst equation should be evaluated in terms of activities and fugacities rather than concentrations and pressures. Since the activity coefficients for peroxide ion are unknown, it did not seem appropriate to correct the other two factors. Also the concentration of peroxide ion should be expressed in molalities rather than molarities but the error caused is too small to be worth correcting.

Having shown how to calculate the electromotive force of an air-depolarized cell for any observed current (and corresponding voltage) we need, according to equation 16, the magnitude of R_i in order to test the validity of our calculations. It was thought at first that the internal resistance could be measured by making the cell one branch of an alternating current bridge. Such measurements did indeed show that the internal resistance was a constant independent of current density, but it was found later that the value of R_i obtained in this manner was lower than the "direct current resistance." The reason is apparently connected with the previously mentioned resistance barrier peculiar to gas electrodes (11). To circumvent this difficulty we have assumed a reasonable value for R_i and have shown that the calculated voltages check the observed ones closely for all current densities. Having done this for two different cells with widely different internal resistances, we feel we have justified our assumption that the potential of the air electrode is determined solely by the oxygen-peroxide equilibrium at all current densities. The data are presented in Fig. 3.

With the exception of the two points near the region of diffusion-limited current in Cell I, the observed voltages average 0.02 volts higher than calculated. The observed voltages for Cell II average 0.04 volts lower than calculated. The maximum scatter in either case is about the same—0.03 volts. If we disregard the constant error (different for the two cells), caused perhaps by liquid junction potentials included in the measurement of $E_{Zn^{++}}$, we see that the calculated curves follow the observed very closely.

Two simple qualitative experiments bearing on the voltage of air-depolarized cells were performed. In the first, a small amount of copper sulfate was added to a model cell delivering 0.090 amps. Since cuprate ion was found (Sec. 3) to be such an excellent catalyst for the decomposition of peroxide ion one would expect an increase in voltage (and therefore current). The current did indeed rise to 0.091 amps and in another test rose from 0.333 to 0.337 amps. In the second qualitative experiment some concentrated hydrogen peroxide was added to a discharging air-depolarized cell. As expected the current and voltage dropped. Recovery to the original condition occurred in about half an hour.

Current-voltage curves for an air-depolarized cell having saturated ammonium chloride for its electrolyte have also been obtained, and a calculation of the electromotive force was attempted. In acid solutions the half cell reaction for the reduction of oxygen to hydrogen peroxide is

$$H_2O_2 \rightleftharpoons O_2 + 2H^+ + 2e \tag{21}$$

and the electromotive force at 25°C. is

$$E = E^0_{H_2O_2} - 0.0295 \log \frac{P_{O_2}[H^+]^2}{[H_2O_2]} . \tag{22}$$

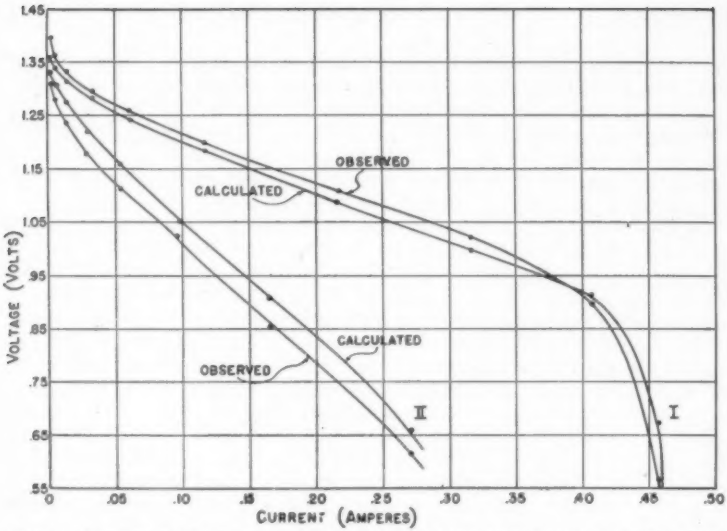

FIG. 3. Current-voltage curves for alkaline air-depolarized cells at 25°C. Cell I: Area of air-depolarizing electrode (A) = 15.1 cm², height of air-depolarizing electrode (x) = 7.35 cm, resistance of cell (R_i) = 0.725 ohm. Cell II: Area of air-depolarizing electrode (A) = 15.8 cm², height of air-depolarizing electrode (x) = 9.1 cm, resistance of cell = 2.05 ohms.

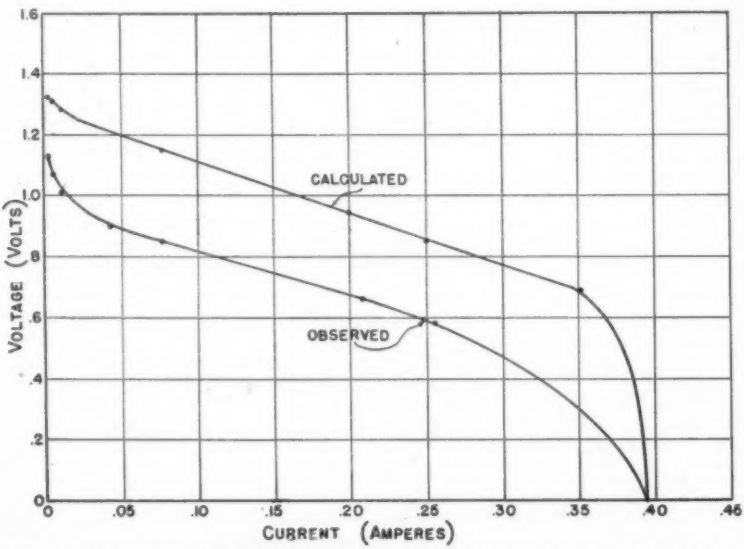

FIG. 4. Current-voltage curve for acidic air-depolarized cell: Area of air-depolarizing electrode (A) = 15.1 cm², height of air-depolarizing electrode (x) = 8.65 cm, resistance of cell = 1.45 ohms, temperature = 30°C.

Again the electromotive force of the zinc-zinc ion couple was measured against a calomel electrode. The hydrogen ion concentration was measured with a pH meter and the other factors calculated as outlined previously. Here a value of $k = 15 \times 10^{-4}$ sec.$^{-1}$ was used to calculate the equilibrium hydrogen peroxide concentrations. Latimer (5) gives -0.682 v as the value for $E^0_{H_2O_2}$. The results of a typical experiment are plotted in Fig. 4. That the observed voltages lie well below (average of 0.26 v below) the calculated is in harmony with the results of the previous sections where it was shown that although oxygen can be reduced to hydrogen peroxide in acidic media (Sec. 2) the reaction is far from reversible (Sec. 1).

CONCLUSIONS

(1) Oxygen is not reversibly reduced to hydrogen peroxide in acidic solutions at a carbon electrode.

(2) In basic solutions peroxide ion cannot be reduced to water at carbon or at mercury electrodes; in acidic solutions hydrogen peroxide is readily reduced. When oxygen is also present, however, its reduction always takes precedence.

(3) The rate of decomposition of peroxide in alkaline and in acidic air-depolarized cells has been measured, and it has been shown that peroxide is removed from such a cell by catalytic decomposition only. The rate of formation of peroxide is in accordance with Faraday's laws, indicating that it is the primary product from the reduction of oxygen.

(4) The mechanism by which oxygen is transported through an air-depolarizing electrode has been shown to be diffusion and the diffusion coefficient has been measured.

(5) The potential of an alkaline air-depolarizing electrode discharging at all current densities is a function of the peroxide ion concentration as required by the Nernst equation.

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Any discussion of this paper will appear in the discussion section of Volume 93 of the Transactions of the Society.

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